2018

Development of high performance liquid chromatography compatible microextraction techniques using ionic liquids as extraction solvents

Jiwoo An
Iowa State University

Development of high performance liquid chromatography compatible microextraction techniques using ionic liquids as extraction solvents

by

Jiwoo An

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Analytical Chemistry

Program of Study Committee:
Jared L. Anderson, Major Professor
R. Samuel Houk
Thomas A. Holme

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2018

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ACKNOWLEDGMENTS

I would like to first extend my sincere gratitude to Dr. Jared Anderson for providing me with an opportunity to work in this laboratory for the past 3 years. I want to also thank him for his guidance and teaching, for his curiosity and enthusiasm in science. The last 3 years spent in his laboratory has been a life-changing and an extraordinary learning experience. I would also like to thank my committee members, Drs. R. Samuel Houk and Thomas Holme for their support and guidance.

I would like to extend my gratitude to all of my former and current group members: Honglian Yu, Josias Merib, Cheng Zhang, Omprakash Nacham, Kevin Clark, He Nan, Stephen Pierson, Jeff Purslow, Marcelino Varona, Ashley Bowers, Miranda Emaus, Gabriel Odugbesi, Chenghui Zhu, Qamar Farooq, along with all visiting professors and postdoctoral fellows: Drs. Cecilia Cagliero, Dongmei Lu, Kosuke Kuroda, Xi-Tian Peng, María José Trujillo-Rodríguez, Xiong Ding, and Deepak Chand for encouragements and criticisms.

I would like to express my most sincere thanks to my families, in S. Korea (my parents and my brother) and in the U.S. (mom and dad Quittem, Amanda, John, Jessica, and Erica), for their continuous support and love, as I could have not finished this journey without them. I would also like to thank the most special people in my life, Andrew Pierson and Melanie Gibbons, who have been with me every step of the way, through good and bad.

Lastly, I would like to thank my friends and the department faculty and staff at Iowa State University for their support.

CHAPTER 1

INTRODUCTION

1.1 Introduction to microextraction techniques

Sample preparation step is an essential part of the analytical process. It typically involves an extraction procedure that allows separation and/or preconcentration of target compounds from a sample matrix [1]. Many traditional extraction procedures such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are typically not only labor-intensive and time consuming, but they are often faced with low yield and high consumption of hazardous organic solvents. Though the traditional extraction methods are still beneficial and useful in some analyses, their distinct disadvantages have led to development of more efficient and miniaturized sample preparation techniques.

Numerous miniaturized extraction procedures have been introduced in the past few decades. Liquid-phase microextraction (LPME) techniques involve the use of liquid solvents as extraction phase, and examples of these methods include dispersive liquid-liquid microextraction (DLLME) and single-drop microextraction (SDME). The LPME methods are widely utilized in many laboratories due to the simple, efficient, rapid, and inexpensive nature of the techniques. In addition, LPME techniques generally require very low amounts of organic solvent, which help with reduction of toxic organic waste.

In DLLME, extraction is performed based on ternary solvent system. A mixture of extraction and disperser solvent is introduced to a sample solution creating a cloudy solution, and the extraction phase is later separated from the sample solution by centrifugation [2]. Representative examples include microwave-, ultrasound-, and vortex-assisted DLLME methods. The common objective of these methods is to increase preconcentration by increasing

surface contact area of extraction phase and the sample solution [3]. Another main element of LPME is SDME, which utilizes a single droplet of solvent suspended on the needle of a syringe as extraction phase [4]. The SDME technique is generally divided into two different modes – headspace (HS) and direct-immersion (DI). Determination of wide classes of compounds, including volatile, semi-volatile, and non-volatile, is possible when the appropriate mode of SDME is used. Figure 1 represents the general setup of SDME method.

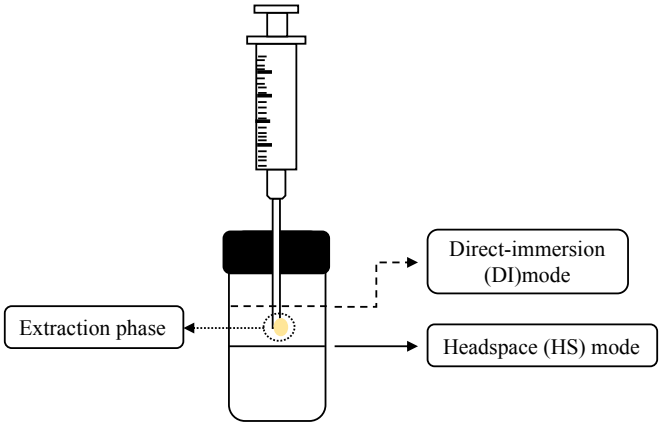

Figure 1. Schematic of SDME method.

Solid-phase microextraction (SPME), on the other hand, utilizes coated fibers as extraction phase [5]. Generally, two steps are involved in the SPME procedure – extraction and desorption of analytes. Analyte partitioning from the sample matrix to the extraction phase is the basic principle of SPME technique, and different types of sorbent materials are used for different classes of analytes [6]. The rapid sampling is possible as SPME is a non-exhaustive extraction technique, and similar to SDME, two modes of extraction (HS and DI) are widely used. Finally, analytes are either desorbed by applying high temperatures or by exposing the sorbent coating to a small volume of appropriate solvent. A general process of SPME can be seen in Figure 2.

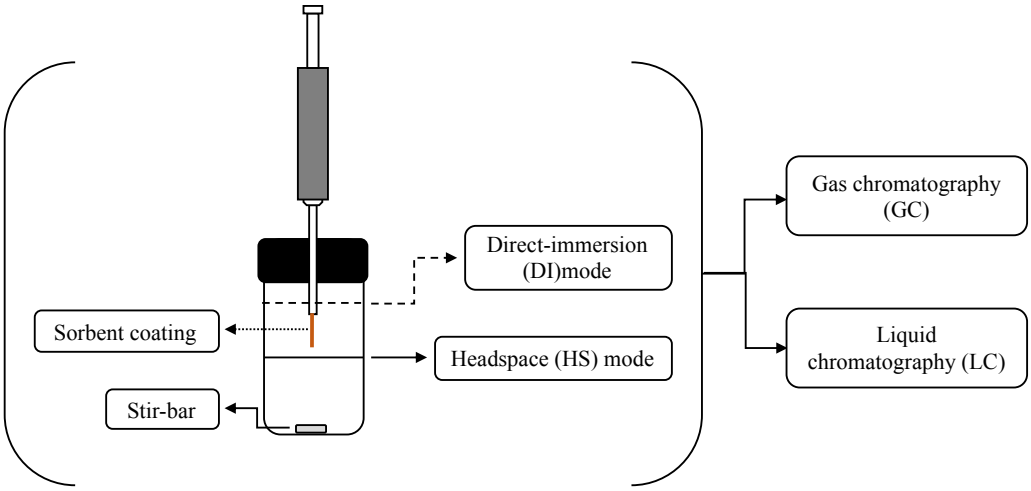

Figure 2. Schematic of a typical SPME procedure.

1.2 Ionic liquids and their application in microextraction techniques

Ionic liquids (ILs) are generally described as non-molecular molten salts possessing melting points at or below 100 °C [7]. In addition to their low melting points, ILs typically possess low vapor pressure and a wide range of solubility, density, viscosity, and refractive index [8]. ILs are also called 'designer solvents' due to the fact that their structures can be tailored to modify the physicochemical properties. Incorporation of a paramagnetic metal ion in either cationic or anionic component of the IL structure results in a subclass of ILs called magnetic ionic liquids (MILs), which possess some degree of magnetic susceptibility [9]. These compounds still possess advantages of conventional ILs, but they also can be manipulated by applying an external magnetic field [10]. Another known subclass of ILs, polymeric ionic liquids (PILs), are composed of a polymerizable functional group in addition to typical cationic and anionic components [11]. Some of the common structures of ILs can be seen in Figure 3.

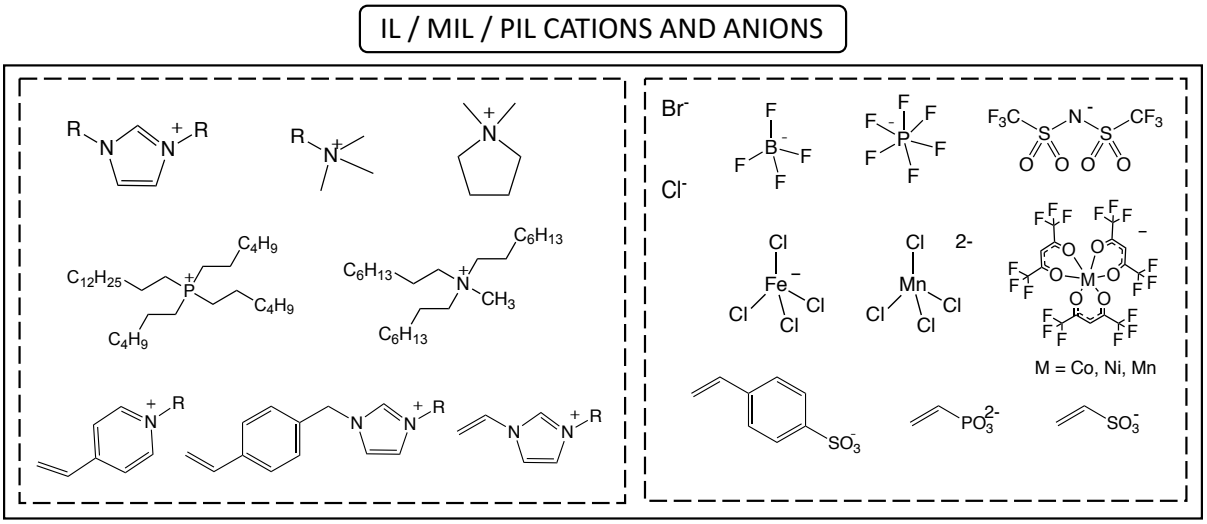

Figure 3. Common cations and anions used in ILs, MILs, and PILs.

Many studies have utilized ILs in sample preparation techniques as alternative solvents to traditional organic solvents. Conventional ILs such as 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM^+][PF_6^-]$) or the same cation paired with bis[(trifluoromethyl)sulfonyl]imide ($[NTf_2^-]$) anion are widely used in both DLLME and SDME methods. [3]. MILs have relatively fewer reports in their application to microextraction techniques. However, a few studies have reported the use of MILs such as 1-butyl-3-methylimidazolium tetrachloroferrate (III) ($[C_4MIM^+][FeCl_4^-]$) [12], trihexyl(tetradecyl)phosphonium tetrachloroferrate $[P_{6,6,6,14}^+][FeCl_4^-]$ [13], and trihexyl(tetradecyl)phosphonium tetrachloromanganate $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ [14, 15]. The application of PILs is much more common in SPME, where the compounds are used as selective sorbent coatings for targeted extraction from sample solutions. Some examples include extraction of deoxyribonucleic acid (DNA) [16], fatty acid methyl esters [17], and phthalate esters [18].

When ILs are used as extraction phases in microextraction, direct coupling to chromatographic instruments is also possible. Coupling of developed IL-microextraction

methods with gas-chromatography (GC) [19] or high-performance liquid chromatography (HPLC) [20] is common, and more highly sensitive detection techniques such as mass spectrometry (MS) can be paired with chromatographic instruments [21].

1.3 Organization of the thesis

The main goal of this thesis was to extend the use of ILs, specifically MILs and PILs, in microextraction procedures for the monitoring of organic compounds, and in combination with chromatographic techniques. According to this main objective, the present thesis has been divided in the following chapters:

Chapter 2 describes the development of a MIL-HS-SDME method in combination with HPLC for determination of twelve aromatic compounds. A magnetic rod was utilized to suspend the MIL droplet, which greatly increased the droplet stability in high temperature conditions. The analyte-enriched MIL droplet was directly injected into HPLC without further clean-up procedure, allowing simple and straightforward analysis.

Chapter 3 describes the development of double-confined PIL sorbent coating to be used in SPME platform in combination with HPLC for the analysis of ultraviolet filter compounds. PIL monomer and crosslinker were synthesized and polymerized to create an extremely stable PIL-based sorbent coating which underwent approximately 120 extractions in sample solution containing 25% sodium chloride (NaCl, w/v). The developed double-confined PIL sorbent coating exhibited much longer lifetime and similar extraction capabilities in comparison to a widely used commercial sorbent coating.

Chapter 4 provides a short summary of the completed research projects.

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CHAPTER 2

HEADSPACE SINGLE DROP MICROEXTRACTION VERSUS DISPERSIVE LIQUID-LIQUID MICROEXTRACTION USING MAGNETIC IONIC LIQUID EXTRACTION SOLVENTS

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Jiwoo An, Kira L. Rahn, and Jared L. Anderson

Abstract

A headspace single drop microextraction (HS-SDME) method and a dispersive liquid-liquid microextraction (DLLME) method were developed using two tetrachloromanganate ($[MnCl_4^{2-}]$)-based magnetic ionic liquids (MIL) as extraction solvents for the determination of twelve aromatic compounds, including four polyaromatic hydrocarbons, by reversed phase high-performance liquid chromatography (HPLC). The analytical performance of the developed HS- SDME method was compared to the DLLME approach employing the same MILs. In the HS- SDME approach, the magnetic field generated by the magnet was exploited to suspend the MIL solvent from the tip of a rod magnet. The utilization of MILs in HS-SDME resulted in a highly stable microdroplet under elevated temperatures and long extraction times, overcoming a common challenge encountered in traditional SDME approaches of droplet instability. The low UV absorbance of the $[MnCl_4^{2-}]$-based MILs permitted direct analysis of the analyte enriched extraction solvent by HPLC. In HS-SDME, the effects of ionic strength of the sample solution, temperature of the extraction system, extraction time, stir rate, and headspace volume on extraction efficiencies were examined. Coefficients of determination (R^2) ranged from 0.994 to 0.999 and limits of detection (LODs) varied from 0.04 to 1.0 μg L^-

[1] with relative recoveries from lake water ranging from 70.2 % to 109.6 %. For the DLLME method, parameters including disperser solvent type and volume, ionic strength of the sample solution, mass of extraction solvent, and extraction time were studied and optimized. Coefficients of determination for the DLLME method varied from 0.997 to 0.999 with LODs ranging from 0.05 to 1.0 μg L^{-1}. Relative recoveries from lake water samples ranged from 68.7 % to 104.5 %. Overall, the DLLME approach permitted faster extraction times and higher enrichment factors for analytes with low vapor pressure whereas the HS-SDME approach exhibited better extraction efficiencies for analytes with relatively higher vapor pressure.

2.1 Introduction

Sample pretreatment and preconcentration are widely recognized as bottlenecks in the sample preparation of analytes within complex matrices [1]. Many extraction techniques have been developed in the past several decades to preconcentrate target analytes. However, the need for faster, cost-effective, and convenient methods which are capable of high-throughput analysis are still in demand. Traditional sample preparation methods such as liquid-liquid extraction (LLE) often involve tedious and labor-intensive procedures as well as require large volumes of toxic organic solvents [2, 3]. Miniaturized LLE techniques, often referred to as liquid-phase microextraction (LPME), have been introduced in efforts to overcome the disadvantages of conventional sample preparation systems [4-6].

Dispersive liquid-liquid microextraction (DLLME) and single drop microextraction (SDME) are two widely used microextraction techniques. DLLME was first introduced by Rezaee and co-workers in 2006 as a simple extraction method that allows preconcentration of organic compounds by dispersing a water-immiscible organic solvent [7]. Once a mixture of

disperser solvent and extraction solvent is added to an aqueous sample, a cloudy solution is formed. The high surface area of the extraction solvent facilitates rapid extraction of analytes [2, 7]. SDME, introduced in 1996 by Liu and Dasgupta, utilizes a micro-liter volume of a single organic droplet to preconcentrate analytes [8, 9]. SDME can be employed in the direct-immersion (DI) or headspace (HS) modes, depending largely on the types of analytes being extracted and the complexity of the matrix [10]. In DI-SDME, the extraction solvent droplet is directly immersed in the sample solution, enabling extraction of non-volatile compounds. On the other hand, HS-SDME is useful for the extraction of volatile or semi-volatile compounds from complex sample matrices as the analytes are extracted from the headspace above the sample solution [5, 11].

In an effort to investigate alternative solvent systems for DLLME and SDME, ionic liquids (ILs) have enjoyed increasing popularity due to their unique properties [5, 12-14]. The chemical structures of IL cations and anions can be tailored to impact a number of unique physicochemical properties including low or negligible vapor pressure at room temperature, high thermal stability, and variable viscosity. One of the more appealing characteristics of ILs in analytical chemistry is that they can be designed for specific applications [15]. Within the past decade, ILs have been successfully applied to DLLME and SDME methods for the analysis of a wide range of analytes including polycyclic aromatic hydrocarbons (PAHs) [12, 16, 17], insecticides [14], pesticides [18, 19], phenols [20, 21], and metals [22-24]. Magnetic ionic liquids (MILs) are a subclass of ILs that exhibit paramagnetic behavior due to the incorporation of either paramagnetic cations or anions in their structures, allowing them to be readily manipulated through the use of an applied magnetic field. MILs have received an increasing amount of attention as solvent systems in various of analytical techniques [25].

When used as extraction solvents in microextraction techniques, MILs provide important advantages that conventional ILs cannot offer. For example, the centrifugation step in DLLME, which is typically required to achieve phase separation between the aqueous sample solution and the extraction phase, can be eliminated by simply retrieving the dispersed MIL microdroplets through the use of a magnet [26, 27]. The elimination of the centrifugation step greatly reduces the analysis time and opens up the prospects of creating entirely automated methods. In HS- SDME, droplet stability is an inevitable issue due to a small surface area of the microsyringe needle tip which holds the microdroplet. In addition, organic solvents with high boiling points may still possess some volatility, especially at high extraction temperatures, leading to loss of extraction solvent volume over long extraction times [11]. Therefore, applying MILs in HS- SDME may provide advantages leading to improvement over existing methods.

There are few reported studies using MILs as extraction solvents [26-31]. The majority of the studies were performed with MILs containing the Fe(III) anion ($[FeCl_4^-]$), which is susceptible to hydrolysis in aqueous solutions and exhibits high absorption in the ultraviolet (UV) region [32-35]. These characteristics not only present difficulties in designing simple extraction procedures, but they also limit the choice of detection method. For example, high UV absorbance may interfere with analyte detection when high-performance liquid chromatography (HPLC) coupled to UV detection is used. Recently, MILs containing the tetrachloromanganate anion ($[MnCl_4^{2-}]$) were utilized as extraction solvents in DLLME coupled to HPLC, taking advantage of the low UV absorbance exhibited by this anion [27]. However, the $[MnCl_4^{2-}]$-based MILs have not been well studied and have not been applied in

other extraction systems. Thus, further studies into the use of MILs in microextraction techniques is important in order to improve existing methods.

In this study, we present for the first time a HS-SDME method which utilizes two [$MnCl_4^{2-}$]-based MILs, namely, trihexyl(tetradecyl)phosphonium tetrachloromanganate ([$P_{6,6,6,14}^{+}$]$_2$[$MnCl_4^{2-}$]) and aliquat tetrachloromanganate ([$Aliquat^{+}$]$_2$[$MnCl_4^{2-}$]) coupled to HPLC. The two cations have been previously shown to exhibit different extraction efficiencies despite small differences in their chemical structure when used in DLLME [27]. They have never been explored in any SDME platform. The [$MnCl_4^{2-}$]-based MILs exhibit no sign of hydrolysis in aqueous solution unlike the [$FeCl_4^{-}$]-based MILs, enabling sampling without pH adjustment. In addition, the low UV absorbance of the [$MnCl_4^{2-}$]-based MILs permits direct analysis of the extraction solvent by HPLC-UV. Similar MILs have also been applied in studies employing high ionic strength solutions, demonstrating their stability in the presence of salts [26, 27, 30]. When MILs are applied as extraction solvents in HS-SDME, the magnetic force maintains the microdroplet on the magnet support throughout the long extraction time as opposed to the droplet being suspended on the tip of a microsyringe needle. Hence, the use of magnet can significantly increase the droplet stability, overcoming a main disadvantage of traditional HS-SDME. Moreover, the loss of extraction solvent due to evaporation is greatly reduced, as the MILs inherently possess low vapor pressure. Following extraction, the analyte enriched MIL droplet was directly subjected to chromatographic analysis by HPLC. The analytical performance of the HS-SDME method using MILs was compared to that of a DLLME method in which MILs are used as the dispersive extraction solvent for the determination of various organic compounds. This study highlights the tremendous applicability of MILs in the field of sample preparation.

2.2 Experimental

2.2.1 Reagents

Aliquat 336 (average molecular weight: 442.00) was purchased from Acros Organics (Pittsburgh, PA, USA). Trihexyl(tetradecyl)phosphonium chloride (97.7%) was purchased from Strem Chemicals (Newburyport, MA, USA). Manganese (II) chloride tetrahydrate (98.0%) was purchased from Alfa Aesar (Ward Hill, MA, USA). The analytes acetophenone (99.0%), 2-chloroaniline (>98.0%), α,α,α-6-tetrafluoro-m-toluidine, 4-chlorobutyrophenone, benzophenone (99.0%), 2-nitronaphthalene (85.0%), biphenyl (99.5%), α,α,α-trichlorotoluene (98.0%), and 1-chloro-4-nitrobenzene (99.0%) were purchased from Sigma Aldrich (St. Louis, MO, USA). The analyte 2-bromo-4-fluorobenzaldehyde (99.0%) was purchased from Oakwood Products, Inc. (West Columbia, SC, USA) and fluorene, phenanthrene, and anthracene with purities greater than 96.0% were purchased from Supelco (Bellefonte, PA, USA). Sodium chloride was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Acetonitrile, acetone, and methanol (≥99.9%) were purchased from Sigma Aldrich. Neodymium rod magnets (0.66 T) were purchased from K&J Magnetics (Pipersville, PA, USA). Ultrapure water (18.2 MΩ cm) was produced by a Milli-Q water filtration system (Millipore, Bedford, MA, USA) and was used for the preparation of all solutions.

All analytes and their physical and chemical properties are listed in Table A1 (Appendix A). Individual stock solutions were prepared at 5000 mg L^{-1} in acetonitrile for each analyte, except for the stock solution of anthracene, which was prepared at 1000 mg L^{-1}. A working solution containing all twelve analytes was prepared at 200 mg L^{-1} in acetonitrile, with the exception of α,α,α-6-tetrafluoro-m-toluidine and biphenyl (100 mg L^{-1} and 40 mg L^{-}

[1], respectively). For consistency, the same working solution was used for the DLLME and HS-SDME methods. Aqueous samples were prepared fresh before each extraction by spiking an appropriate amount of working solution into a 30% NaCl (w/v) aqueous solution.

2.2.2 Instrumentation

An Agilent 1260 Infinity HPLC system (Santa Clara, CA, USA) equipped with a quaternary pump, a manual injector, and a diode array detector was used for chromatographic analysis after DLLME. A Shimadzu LC-20A system (Shimadzu, Japan) consisting of a manual injector, a DGU-20A_3 degasser, two LC-20AT pumps, and a SPD-20 UV/Vis detector was used for separation of analytes after HS-SDME. All separations were performed using a Restek Ultra II C18 column (250 mm x 4.6 mm, 5.0 um, State College, PA, USA). Ultrapure water and acetonitrile were utilized as mobile phases for the separation of all compounds. The gradient separation was started and held at 53% acetonitrile for 10 minutes, and increased to 80% over 20 minutes, followed by an immediate increase in acetonitrile to 100% for 10 minutes. All analytes were detected at 254 nm.

Viscosity measurements of the MILs were performed using a Wells/Brookfield DV1 cone and plate viscometer with a CPA-51Z cone spindle at ambient temperature (21.4°C). Both MILs were dried in a vacuum oven at 50°C for 12 hours prior to the measurement in order to ensure complete removal of water and residual solvents. A sample volume of 0.5 mL was used for each MIL.

2.2.3 Synthesis and characterization of magnetic ionic liquids

The two magnetic ionic liquids, $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ and $[Aliquat^{+}]_2[MnCl_4^{2-}]$, were synthesized using a previously reported procedure [36, 37] with slight modifications. Briefly, a 0.5 molar equivalent of $MnCl_2{\cdot}4H_2O$ was added to a methanolic solution of

$[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$. The reaction was stirred at room temperature for 24 h, and the solvent was removed by rotary evaporation. The resulting product was dried overnight in a vacuum oven at 50°C. Complete characterization of these MILs was reported recently by our group [27]. The $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL exhibited a viscosity of 91030 cP at 21.4 °C, which falls within the previously reported viscosity values of 112300 cP (20°C) and 75230 cP (25°C) [36]. The viscosity of the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL exceeded the working range of the instrument (103500 cP).

2.2.4 Method optimization

Several extraction parameters were optimized for the DLLME method using both MILs. For the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, the disperser solvents acetonitrile, acetone, and methanol were examined. The effects of MIL mass (5 to 20 mg), extraction time (30 s to 120 s), disperser solvent volume (5 to 20 µL), and salt concentration (0 to 30% NaCl (w/v)) were subsequently studied. For the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL, optimization of disperser solvent type, disperser solvent volume, and extraction time were performed using the same conditions applied for the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL.

In the HS-SDME experiments, the amount of salt in the aqueous sample (0 to 30% NaCl (w/v)), as well as effect of temperature (20, 40, 60°C), mass of MIL microdroplet (5 to 20 mg), extraction time (5 to 75 min), stir rate (400 to 1100 rpm), and headspace volume (2.5 and 4 mL) were investigated.

2.2.5 Procedures

2.2.5.1 Dispersive liquid-liquid microextraction (DLLME)

The DLLME method was performed by first homogenizing 20 mg of the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL with 20 µL of acetonitrile. The mixture was pipetted into a vial

containing an appropriate concentration of analyte solution made with 6 mL of an aqueous solution of 30% NaCl (w/v). The vial was immediately capped and manually agitated for 2 minutes. A rod magnet (0.66 T) was used to collect the MIL microdroplets from the aqueous solution. The collected MIL was dissolved in 20 μL of acetonitrile and subjected to HPLC analysis. All extractions were performed in 7 mL screw cap glass vials. For the $[Aliquat^+]_2[MnCl_4^{2-}]$ MIL, the same procedure was applied with 5 μL of methanol as disperser solvent and 1 minute of manual agitation.

2.2.5.2 Headspace single drop microextraction (HS-SDME)

In the HS-SDME method, 20 mg of the MIL was held on the bottom of the rod magnet, which was tightly inserted into a PTFE silicone septum of a screw cap. A small stir bar was added to 6 mL of the aqueous sample solution prepared with 30% NaCl (w/v). The vial was capped and the aqueous solution was stirred for 60 minutes at 400 rpm and 800 rpm for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ and the $[Aliquat^+]_2[MnCl_4^{2-}]$ MILs, respectively. The extraction temperature was kept at 60°C for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL and 40°C for the $[Aliquat^+]_2[MnCl_4^{2-}]$ MIL. Stir bars and rod magnets were washed with acetonitrile, acetone, and deionized water following the extractions to minimize any carryover effects. The analyte enriched MIL microdroplet was dissolved in 20 μL of acetonitrile and subjected to HPLC analysis.

2.2.5.3 Method validation

The analytical performance of the optimized method was evaluated in ultrapure water. A calibration curve for each analyte was obtained by examining peak areas of extracted analytes at different concentration levels. The LOD was determined by decreasing the analyte concentration until a signal to noise ratio of 3 was acquired. Lake water was collected from a

local lake (Ames, IA, USA) and used to evaluate the relative recovery of analytes. Nylon filters (0.45 μm) were used to filter the water samples prior to all extractions.

2.3 Results and discussion

2.3.1 Optimization of the DLLME method

Several parameters for the DLLME method including the disperser solvent type, mass of MIL, extraction time, disperser solvent volume, and the ionic strength of the aqueous sample solution were optimized using a factor by factor approach. The optimization was originally performed with the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL. A disperser solvent is used in DLLME to assist in creating fine microdroplets of the extraction solvent within the sample solution. An ideal disperser solvent should be miscible with both the extraction solvent and the sample matrix [21]. In this study, acetonitrile, methanol, and acetone were examined as disperser solvents. Acetonitrile provided the highest peak areas for most of the analytes, whereas acetone resulted in the lowest peak areas for all analytes except anthracene (see Figure A1 of Appendix A). In addition, a lower precision was observed when acetone was used as dispersive solvent, with relative standard deviation (RSD) values varying from 4.6% to 24.7%. Thus, acetonitrile was selected as disperser solvent for the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL.

In order to study the effect of extraction solvent mass on extraction efficiencies, four different masses (5, 10, 15, 20 mg) of MIL were examined. Higher extraction efficiencies were observed for all analytes when the mass of MIL was increased up to 15 mg, as shown in Figure A2. Further increasing the MIL mass to 20 mg provided a significant increase in peak areas for fluorene, phenanthrene, and anthracene, whereas comparable peak areas were observed for all other analytes. The increase in extraction efficiency with higher mass of MIL may be the

result of more droplets forming during the extraction, while the solubility of the droplets is minimized by the use of hydrophobic MILs. Similar observations were made in previous DLLME studies [19, 31, 38]. Therefore, a mass of 20 mg was used for all subsequent extractions.

As the extraction solvent is dispersed into fine droplets within the sample solution, analyte molecules quickly partition into the extraction phase due to the high surface area of the extraction solvent [12]. Extraction time is an important variable in DLLME as a sufficient amount of time should be given to allow equilibration between the sample solution and the extraction solvent. Extraction times from 30 to 120 seconds were examined in this study. Sorption-time profiles for the DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL are represented in Figure 1. A steady increase in peak area was observed for acetophenone, 1-chloro-4-nitrobenzene, 2-nitronaphthalene, benzophenone, and phenanthrene when the extraction time was increased from 30 s to 120 s. Profiles of 2-chloroaniline, α,α,α-6-tetrafluoro-m-toluidine, fluorene, and anthracene plateaued following an extraction time of 90 s, and a similar observation can be made for 2-bromo-4-fluorobenzaldehyde, 4-chlorobutyrophenone, and biphenyl. In order to find the optimal extraction time for all analytes while maintaining high enrichment factors, an extraction time of 120 s was selected for the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL.

The influence of the disperser solvent volume was also evaluated. The use of high volumes of disperser solvent may increase the solubility of analytes in the organic solvent, whereas insufficient volumes of disperser solvent can result in poor dispersion of the extraction solvent. In order to assess the effect of disperser solvent volume, acetonitrile volumes from 5

to 20 μL were examined. Figure 2 shows that the disperser solvent volume did not produce a significant difference in extraction efficiencies for those analytes possessing lower molecular

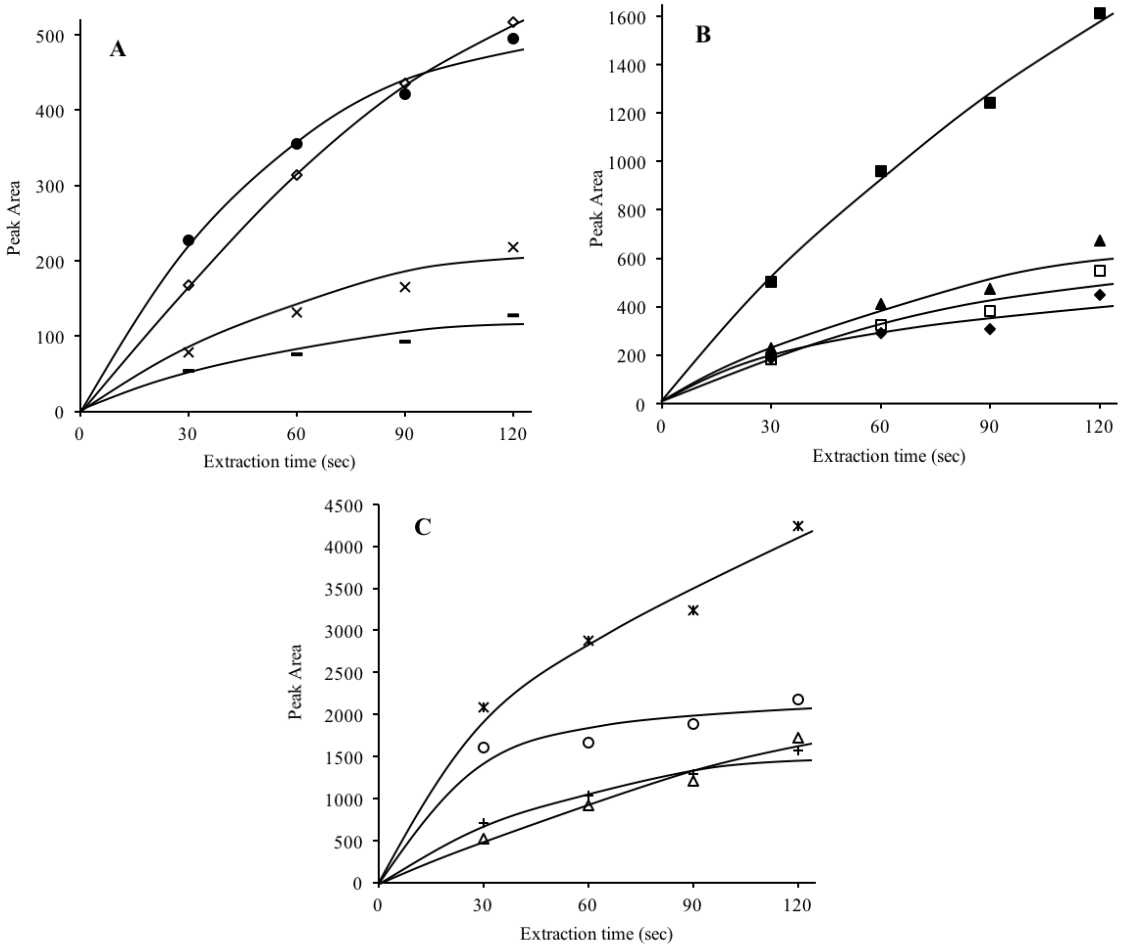

Figure 1. Sorption-time profiles for the DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL. (A) (●) Acetophenone; (×) 2-Chloroaniline; (-) α,α,α-6-tetrafluoro-m-toluidine; (◇) 1-Chloro-4-nitrobenzene; (B) (▲) 2-Bromo-4-fluorobenzaldehyde; (◆) Biphenyl; (□) 4-Chlorobutyrophenone; (■) 2-Nitronaphthalene. (C) (△) Benzophenone; (+) Fluorene; (✶) Phenanthrene; (○) Anthracene. Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Disperser solvent: acetonitrile; MIL mass: 20 mg; Disperser solvent volume: 5 μL; NaCl concentration in the aqueous solution: 0% (w/v).

weight and relatively high volatility. However, the extraction efficiencies of PAHs were greatly affected by the disperser solvent volume. The optimal extraction performance exhibited

by an acetonitrile volume of 20 μL appears to result from a superior dispersion of the MIL in the sample solution.

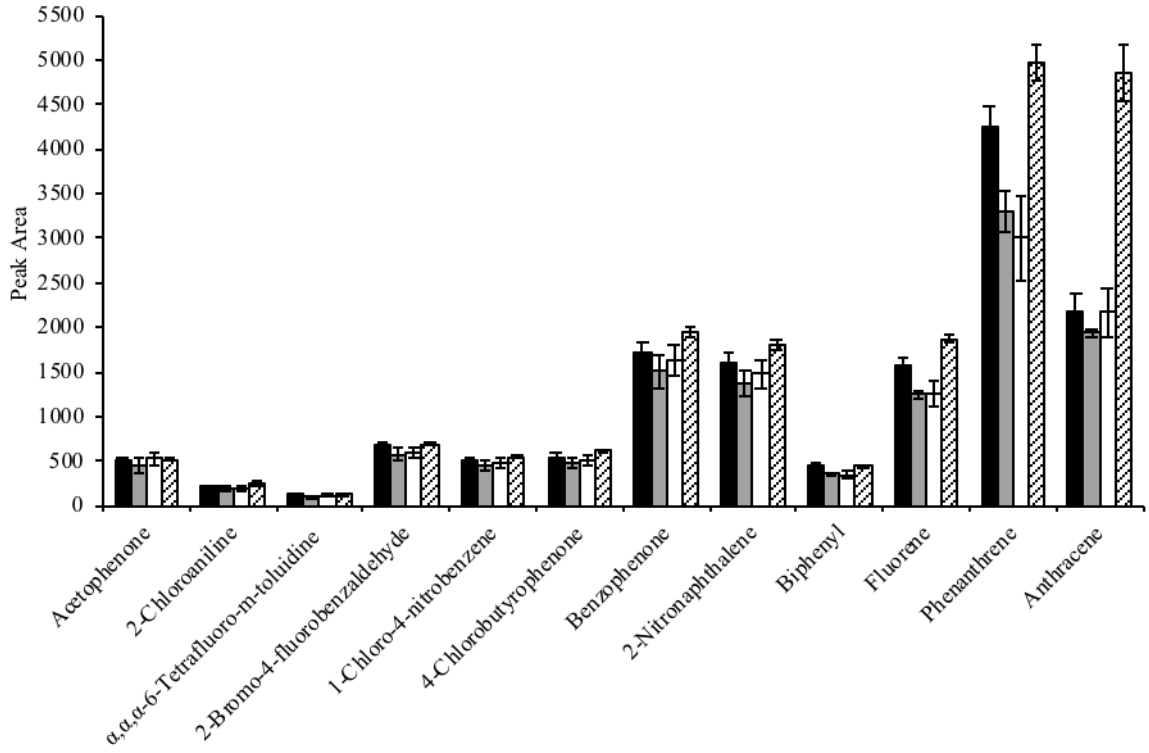

Figure 2. Comparison of disperser solvent volumes for DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL. 5 μL (black bar); 10 μL (gray bar); 15 μL (open bar); 20 μL (dashed bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Disperser solvent: acetonitrile; MIL mass: 20 mg; Extraction time: 120 s; NaCl concentration in the aqueous solution: 0% (w/v).

The addition of kosmotropic salt to the aqueous sample solution prior to extraction can increase analyte extraction efficiencies due to the salting out effect. Elevated concentrations of kosmotropic salts in aqueous solution causes ordering of water molecules and diminished solvation of analytes, resulting in the transfer of analyte molecules to the organic phase, headspace, or extraction phase [39-42]. Therefore, the influence of the ionic strength was examined using NaCl concentrations ranging from 0 to 30% (w/v). In general, higher extraction efficiencies were observed with an increase in the salt concentration, as shown in

Figure A3 of supporting information. Fluorene, phenanthrene, and anthracene exhibited similar or slightly higher peak areas when a 10% (w/v) NaCl solution was used. A slight decrease in peak areas were observed for the three PAHs when the salt concentration was increased from 10 to 20 % (w/v), and those of 30 % (w/v) were comparable to peak areas at 20 % salt content (w/v). One possible reason could be that PAHs, possessing high hydrophobicity and relatively low volatility, may be prone to wall adsorption [43]. In addition, increased extraction efficiencies due to the salting out effect is generally demonstrated more effectively for more polar molecules [4]. To find a compromised extraction condition that provides the optimal extraction efficiencies for most of the studied analytes, a 30% (w/v) NaCl aqueous sample solution was used for subsequent extractions.

Following optimization of the DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, a separate optimization procedure was performed using the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. Based on experimental results obtained from the optimization studies using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, 20 mg of the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL and 30% (w/v) NaCl concentration were applied to all extractions. The remaining parameters, including disperser solvent type, disperser solvent volume, and extraction time were optimized as single variables using the DLLME method.

For the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL, methanol provided the highest peak areas when used as the disperser solvent, as shown in Figure A4. Peak areas for acetophenone, 2-bromo-4-fluorobenzaldehyde, and 1-chloro-4-nitrobenzene were larger using acetonitrile as the disperser solvent, but the differences were not significant. Similar to that of the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, acetone produced not only the lowest extraction efficiencies, but also lower reproducibility compared to methanol and acetonitrile. Therefore, methanol was selected as the disperser solvent for the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL.

The influence of disperser solvent volume was also assessed for the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL by performing extractions using 5 to 20 μL of methanol as disperser solvent. As shown in Figure 3, 5 μL of disperser solvent provided the highest peak areas for all analytes, with the exception of acetophenone. A dramatic decrease in peak area was observed for all analytes other than acetophenone when the disperser solvent volume was increased from 5 to 10 μL, and relatively small increase in extraction efficiencies was obtained when the disperser solvent volume was further increased to 20 μL. Decreased extraction efficiencies have been observed in other studies when high volumes of disperser solvent were used, which lead to increased solubility of the extraction solvent in the aqueous phase [12, 18, 44, 45]. Thus, 5 μL of methanol was chosen as disperser solvent volume for this MIL.

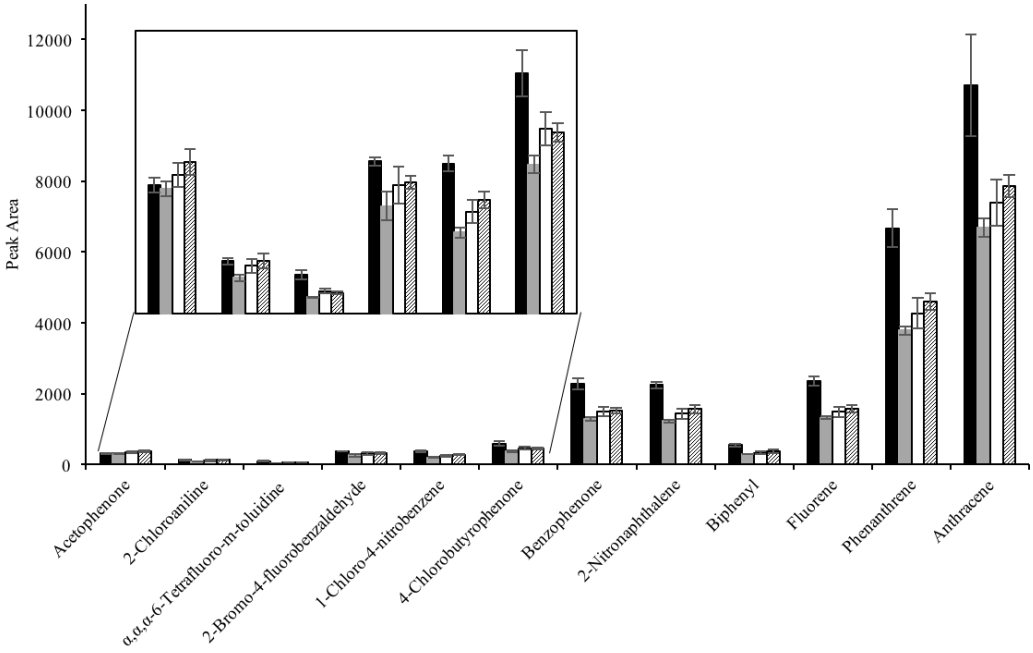

Figure 3. Comparison of disperser solvent volumes for the DLLME method using $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. 5 μL (black bar); 10 μL (gray bar); 15 μL (open bar); 20 μL (dashed bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Disperser solvent: methanol; MIL mass: 20 mg; Extraction time: 60 s; NaCl concentration in the aqueous solution: 30% (w/v).

Extraction times from 30 to 120 seconds were also studied for the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. Unlike the results found with the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, it can be observed in Figure 4 that no notable trend was observed with varying extraction time. Only acetophenone exhibited a continual increase in peak areas with prolonged extraction time, where a maximum peak area was attained at approximately 120 s. For the majority of the analytes, extraction

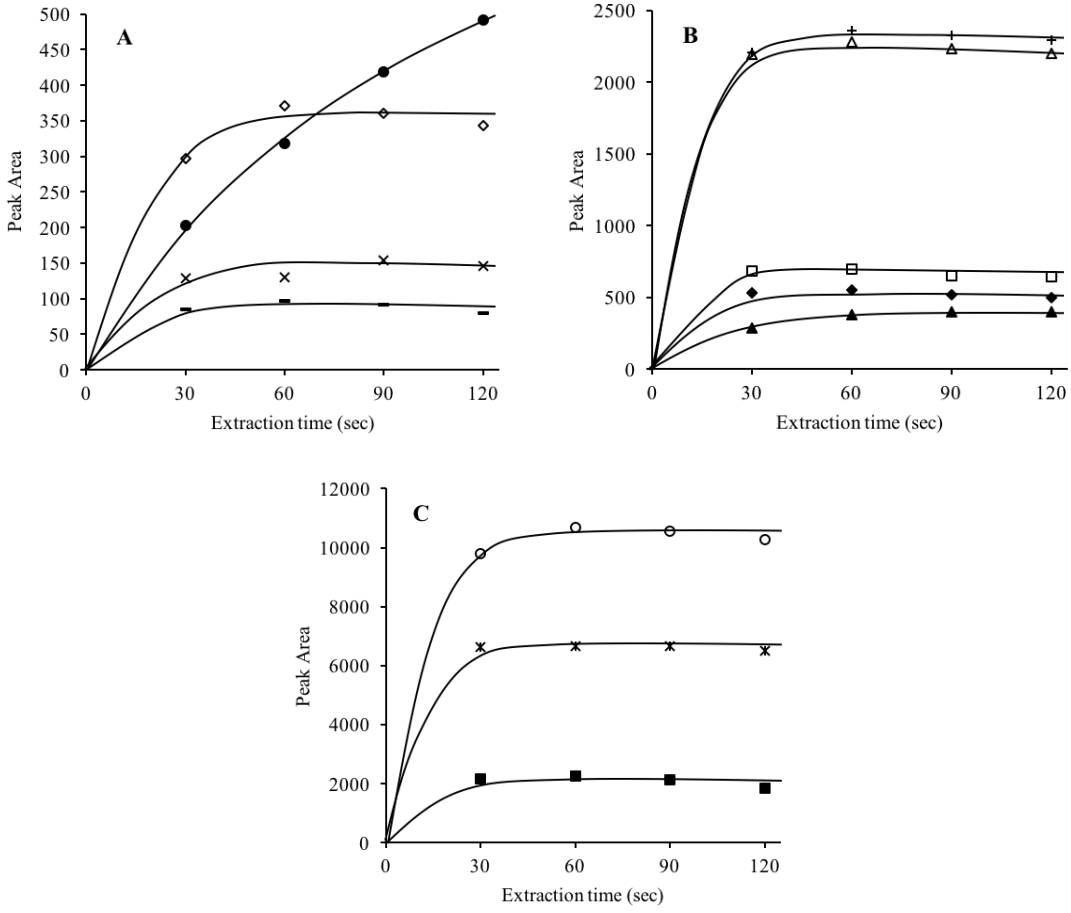

Figure 4. Sorption-time profiles for the DLLME method using $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. (A) (●) Acetophenone; (×) 2-chloroaniline; (-) α,α,α-6-tetrafluoro-m-toluidine; (◇) 1-Chloro-4-nitrobenzene; (B) (▲) 2-Bromo-4-fluorobenzaldehyde; (◆) Biphenyl; (□) 4-Chlorobutyrophenone; (△) Benzophenone; (+) Fluorene. (C) (■) 2-Nitronaphthalene; (✳) Phenanthrene; (○) Anthracene. Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Disperser solvent: methanol; MIL mass: 20 mg; Disperser solvent volume: 5 μL; NaCl concentration in the aqueous solution: 30% (w/v).

times of 60 and 90 s provided similar peak areas. At an extraction time of 120 s, it was observed that the amount of MIL collected by the magnet following extraction was appreciably lower compared to shorter extraction times. Given the aforementioned results, 60 seconds was used for all subsequent extractions with the $[Aliquat^+]_2[MnCl_4^{2-}]$ MIL.

2.3.2 Optimization of the HS-SDME method

The parameters evaluated for the HS-SDME method included: salt concentration in the aqueous solution, temperature of the extraction system, extraction time, stir rate, and headspace volume. These parameters were studied for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ and $[Aliquat^+]_2[MnCl_4^{2-}]$ MILs. The salting out effect for the HS-SDME method was evaluated for aqueous solutions containing 0 to 30% (w/v) of NaCl. The effect of NaCl concentration on the analyte extraction efficiencies for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ and $[Aliquat^+]_2[MnCl_4^{2-}]$ MILs is shown in Figure A5. For both MILs, increased peak areas were observed for the majority of the analytes with an increase in the NaCl concentration. The salting out effect was much less pronounced for phenanthrene and anthracene; in fact, the peak areas were slightly higher for the two PAHs when no salt was added to the aqueous solution. To achieve optimal extraction performance for the majority of analytes, a 30% (w/v) NaCl concentration was chosen for all HS-SDME extractions.

Partitioning of analyte molecules from the aqueous solution to the headspace and from the headspace to the extraction phase is affected by the temperature at which the extraction is carried out [8]. Use of elevated temperature shortens the equilibrium time due to increased diffusion coefficients of the analytes in the liquid phase [46]. Extraction efficiencies of the target analytes were studied by performing extractions at 20°C, 40°C, and 60°C. As shown in Figure 5, all analytes exhibited appreciably higher peak areas for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL

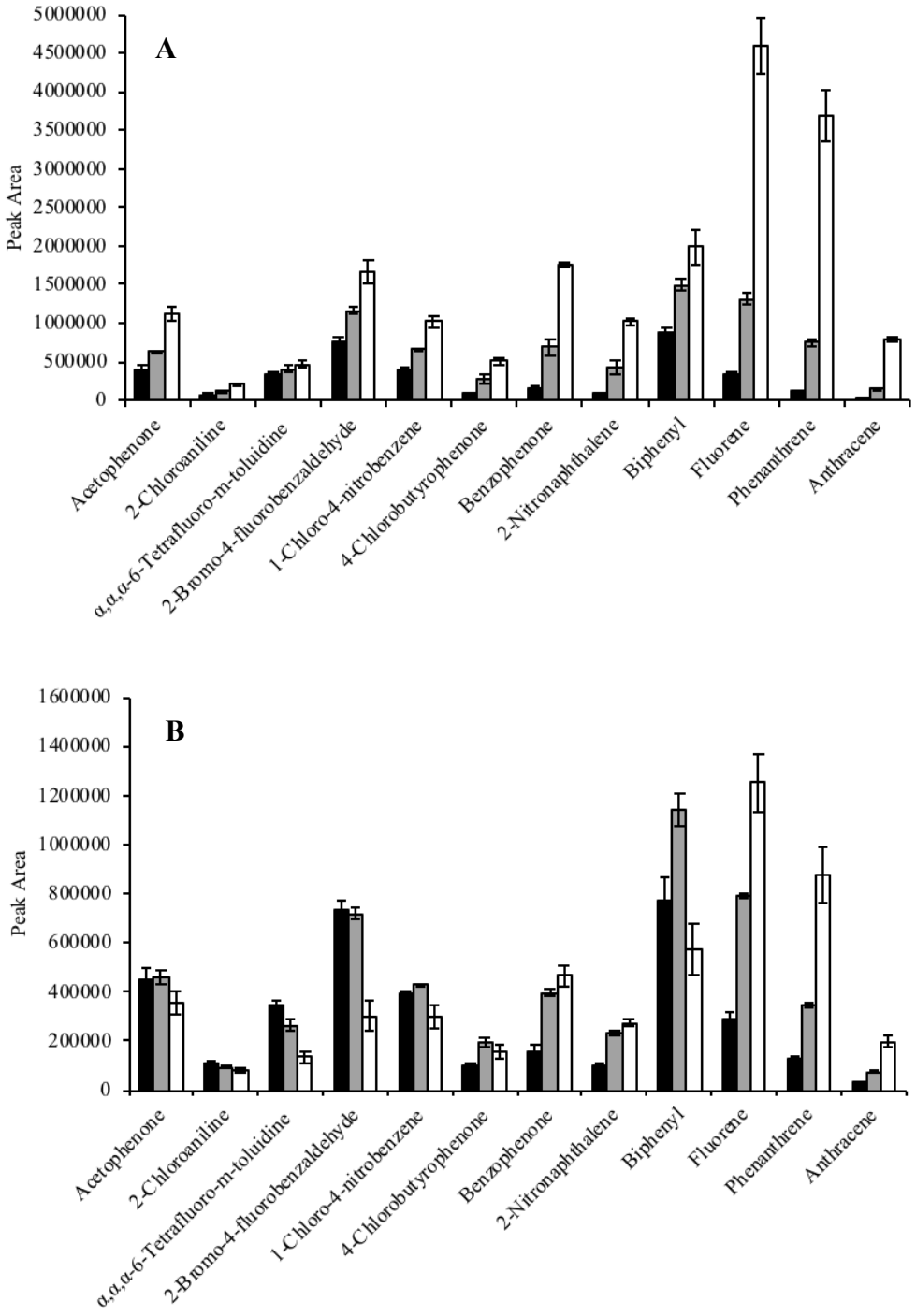

Figure 5. Effect of temperature on extraction efficiencies for the HS-SDME method using (A) $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and (B) $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. 20°C (black bar); 40°C (gray bar); 60°C (open bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; NaCl concentration in the aqueous solution: 30% (w/v); Extraction time: 30 min; MIL mass: 10 mg; stir rate: 800 rpm; headspace volume: 2.5 mL.

when the temperature of the system was increased. PAHs exhibited an especially notable increase in peak area from 40 to 60°C. Interestingly, a different trend was observed for the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL when the temperature was increased. Benzophenone, 2-nitronaphthalene, fluorene, phenanthrene, and anthracene, which possess low vapor pressures, exhibited higher peak areas when an extraction temperature of 60°C was used, whereas other analytes showed either highest extraction efficiencies at 40°C or no discernable difference between 20°C and 40°C. This result indicates that increasing the system temperature not only increases the concentration of analytes in the headspace, but also enhances the partitioning of these analytes into the extraction solvent. However, collecting a consistent amount of the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL was found to be challenging when extractions were performed at 60°C, leading to lower reproducibility. Considering these results, 40°C and 60°C were selected as the optimal extraction temperatures for the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ and the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MILs, respectively.

One of the major advantages of using MILs over traditional organic solvents in SDME is the overall droplet stability. In conventional SDME, a microsyringe is often used to sustain the extraction solvent, in which case the volume of extraction solvent is limited by the small contact area between the syringe tip and the solvent droplet [10]. With MILs, the magnetic susceptibility assists in maintaining the extraction solvent static, which greatly improves the stability of the droplet and permits the use of higher extraction solvent volumes. Theoretically, higher volumes of extraction solvent provide higher enrichment of analytes [9]. The influence of MIL mass was studied by performing extractions using 5, 10, 15, and 20 mg of the MILs. As shown in Figure A6(A) for the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, a larger mass of MIL resulted in

higher peak areas for all analytes, with a significant difference in extraction efficiencies between 5 and 10 mg. On the other hand, the $[Aliquat^+]_2[MnCl_4^{2-}]$ MIL (Figure A6(B)) showed less pronounced differences in extraction efficiencies as the MIL microdroplet mass was increased. Consequently, 20 mg was chosen as the optimum MIL mass for the subsequent experiments.

Extraction time is an important parameter to investigate in SDME to achieve good precision as well as satisfactory enrichment of the analytes as the mass transfer process is dependent on time [10]. In non-exhaustive extraction methods such as HS-SDME, identifying the time in which the three phases attain equilibrium allows for the development of a method to achieve the highest extraction efficiencies [47]. Therefore, extraction times from 5 to 75 minutes were examined. Sorption-time profiles of the analytes are shown in Figure 6 for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ and $[Aliquat^+]_2[MnCl_4^{2-}]$ MILs using the optimal extraction temperatures for each MIL. The analytes with relatively high vapor pressure reached equilibrium within 60 minutes. On the other hand, analytes with higher molecular weight and lower vapor pressure, such as fluorene, phenanthrene and anthracene, exhibited highest extraction efficiencies at 75 minutes. Analytes that possess high molecular weight and low volatility are often expected to require longer time to reach equilibrium in the headspace extraction mode [47]. Therefore, 60 minutes was chosen as the optimal extraction time for both the $[Aliquat^+]_2[MnCl_4^{2-}]$ and the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MILs.

More rapid equilibrium of the analyte between the aqueous sample solution and the headspace can be achieved when higher stir rate is applied [48]. Sufficient agitation should be provided throughout the extraction to promote mass transfer of the target analytes into the headspace. A series of extractions was performed using stir rates of 400, 800, and 1100 rpm.

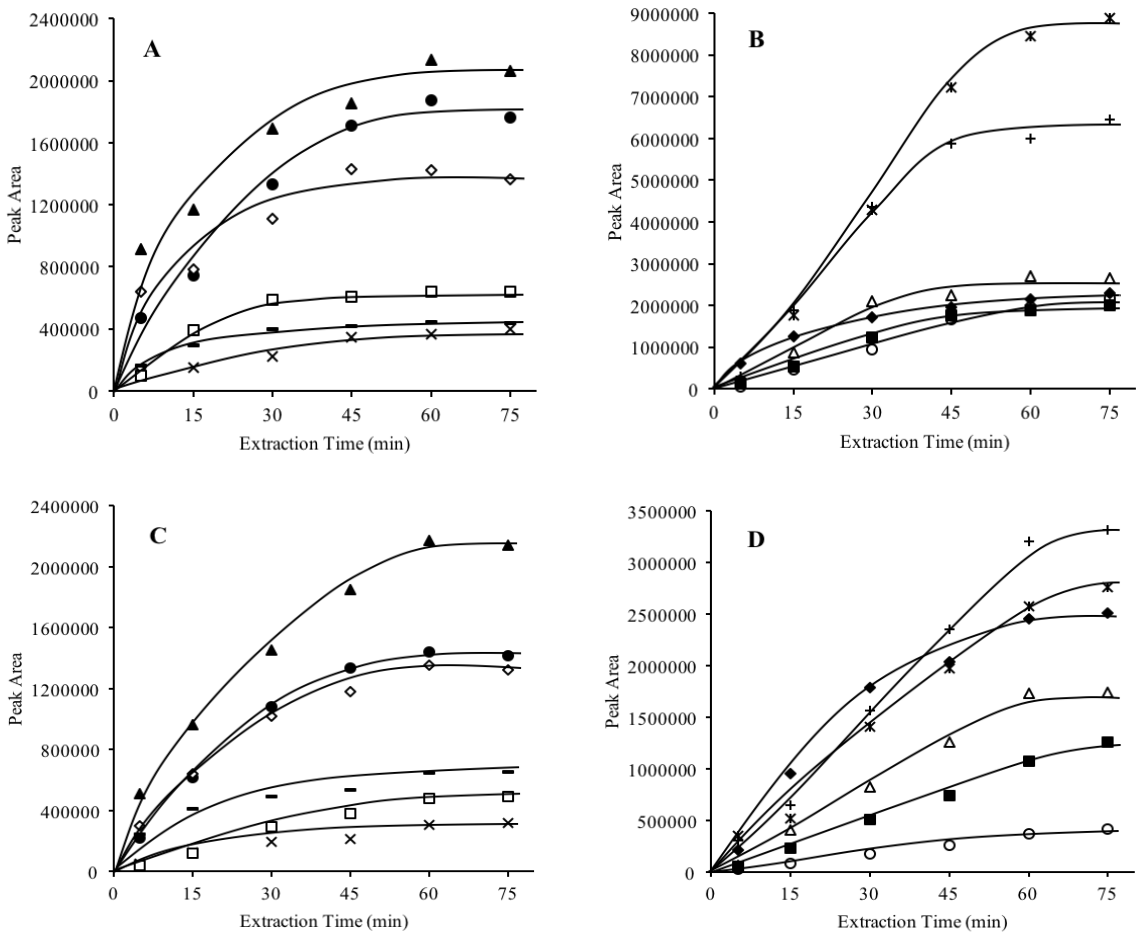

Figure 6. Sorption-time profiles for the HS-SDME method using the (A and B) $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and the (C and D) $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. (●) Acetophenone; (×) 2-chloroaniline; (-) α,α,α-6-tetrafluoro-m-toluidine; (▲) 2-bromo-4-fluorobenzaldehyde; (◇) 1-chloro-4-nitrobenzene; (□) 4-chlorobutyrophenone. (△) benzophenone; (■) 2-nitronaphthalene; (◆) biphenyl; (+) Fluorene; (∗) Phenanthrene; (○) Anthracene. Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; NaCl concentration in the aqueous solution: 30% (w/v); Temperature: 60°C ($[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$), 40°C ($[Aliquat^{+}]_2[MnCl_4^{2-}]$); MIL mass: 20 mg; stir rate: 800 rpm; headspace volume: 2.5 mL.

The lowest stir rate (400 rpm) provided the highest extraction efficiencies for the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, as shown in Figure A7. Extractions performed at 60°C required relatively lower stir rates to provide necessary convection for analytes to reach equilibrium, owing to the fact that the mass transfer rate increases in heated extraction systems [3]. For the

$[Aliquat^+]_2[MnCl_4^{2-}]$ MIL, a higher stir rate (800 rpm) was required to attain the maximum extraction efficiencies. Hence, 400 rpm and 800 rpm were chosen as stir rates for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ and $[Aliquat^+]_2[MnCl_4^{2-}]$ MILs, respectively.

Theoretically, the headspace volume should be kept to a minimum in order to increase extraction efficiency, as increasing the headspace volume consequently decreases the concentration of analytes in the vapor phase [11, 49]. Extractions were performed using headspace volumes of 2.5 mL and 4 mL. A 60 minute extraction time was chosen for the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL at 60°C and for the $[Aliquat^+]_2[MnCl_4^{2-}]$ MIL at 40°C. The aqueous sample volume was kept at 6 mL for consistency. As expected, higher analyte extraction efficiencies were observed for both MILs when a headspace volume of 2.5 mL was employed (see Figure A8). Therefore, a headspace volume of 2.5 mL was employed in further extractions.

2.3.3 Quality parameters and comparison of the methods

Low background absorbance was observed with the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL in the chromatograms shown in Figure A9. Additionally, the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL exhibited higher extraction efficiencies for all analytes compared to the $[Aliquat^+]_2[MnCl_4^{2-}]$ MIL in both DLLME and HS-SDME methods under the optimized conditions. Therefore, the analytical performance of the method was evaluated using the optimized parameters with the $[P_{6,6,6,14}^+]_2[MnCl_4^{2-}]$ MIL based on calibration curves containing eight to eleven concentration levels. The linear range, coefficient of determination (R^2), limits of detection (LOD), and reproducibility were assessed and are reported in Tables 1 and 2. Coefficients of determination (R^2) varied from 0.997 to 0.999 in the DLLME method and from 0.994 to 0.999 in the HS-SDME method. The LODs varied from 0.05 μg L^{-1} to 1.0 μg L^{-1} for the DLLME method and from 0.04 μg L^{-1} to 1.0 μg L^{-1} when the HS-SDME method was used. The reproducibility of

both methods was evaluated at three different spiked concentration levels, namely, 5, 20, and 300 μg L^{-1} (n=3). For the DLLME method, RSDs ranged between 0.3% and 15% at 5 μg L^{-1}. Similarly, RSDs for the HS-SDME method oscillated from 1.8 to 13.8% at 5 μg L^{-1}.

Table 1. Figures of merit for the extraction of twelve analytes by DLLME using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL as extraction solvent[a].

	Linear Range (μg L^{-1})	R^2	Slope ± SD	s_{xy}[b]	LOD (μg L^{-1})	%RSD (n=3)		
						5 μg L^{-1}	20 μg L^{-1}	300 μg L^{-1}
Acetophenone	1-600	0.998	2.734 ± 0.042	24.5	0.5	11.7	13.0	5.8
2-Chloroaniline	0.5-300	0.997	0.751 ± 0.014	4.4	0.05	12.0	13.2	1.2
α,α,α-6-Tetrafluoro-m-toluidine	1-300	0.999	0.565 ± 0.005	1.3	1.0	13.8[c]	0.9[c]	4.9[c]
2-Bromo-4-fluorobenzaldehyde	2-600	0.998	1.966 ± 0.035	20.1	1.0	3.7	14.2	4.4
1-Chloro-4-nitrobenzene	1-600	0.998	1.416 ± 0.022	12.5	0.5	0.3	6.4	0.7
4-Chlorobutyro-phenone	1-600	0.999	1.574 ± 0.011	6.6	0.1	13.7	17.4	2.2
Benzophenone	1-600	0.999	5.203 ± 0.045	26.1	0.5	5.3	5.8	3.5
2-Nitronaphthalene	2-600	0.997	4.462 ± 0.087	48.7	0.2	0.9	5.4	3.1
Biphenyl	0.2-120	0.999	5.569 ± 0.051	5.9	0.1	15.0[d]	5.3[d]	7.1[d]
Fluorene	0.5-600	0.999	6.030 ± 0.065	38.2	0.5	3.8	5.1	3.9
Phenanthrene	1-600	0.999	17.249 ± 0.14	79.9	0.1	1.2	6.9	3.8
Anthracene	0.5-600	0.998	25.873 ± 0.43	250.5	0.1	9.0	8.6	2.0

[a] Conditions: disperser solvent, acetonitrile; MIL mass, 20 mg; extraction time, 120 s; disperser solvent volume, 20 μL; NaCl concentration in aqueous solution, 30% (w/v).
[b] Standard deviation of regression.
[c] Precision at 2.5, 10, and 150 μg L^{-1}.
[d] Precision at 1, 4, and 120 μg L^{-1}.

The enrichment factor (E_F) was used to evaluate the extraction performance of both methods. E_F values were calculated according to Equation 1 below:

$$E_F = \frac{C_{MIL}}{C_{initial}} \quad (1)$$

where C_{MIL} is the concentration of the analytes in the MIL droplet following the extraction and $C_{initial}$ is the initial concentration of analyte in the aqueous solution. C_{MIL} was calculated from calibration curves based on the direct injection of standard solutions. Table 3 lists the calculated E_F values at a spiked concentration of 60 μg L^{-1}. The HS-SDME method using the

Table 2. Figures of merit for the extraction of twelve analytes by SDME using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL as extraction solvent[a].

Analyte	Linear Range (μg L^{-1})	R^2	Slope ± SD	s_{yx}[b]	LOD (μg L^{-1})	%RSD (n=3)		
						5 μg L^{-1}	20 μg L^{-1}	300 μg L^{-1}
Acetophenone	1-300	0.999	3127.4 ± 26.4	8704.1	1.0	13.3	7.0	2.3
2-Chloroaniline	1-300	0.999	786.5 ± 10.5	3164.4	0.2	7.6	6.0	2.6
α,α,α-6-Tetrafluoro-m-toluidine	1-300	0.996	2282.5 ± 56.5	15920.2	0.5	10.2[c]	12.2[c]	3.1[c]
2-Bromo-4-fluorobenzaldehyde	0.5-300	0.996	3396.1 ± 73.7	22763.7	0.5	8.2	8.0	0.9
1-Chloro-4-nitrobenzene	1-300	0.999	2427.6 ± 24.9	7179.6	0.2	9.0	7.6	2.4
4-Chlorobutyro-phenone	2-300	0.998	1295.2 ± 24.5	7062.0	0.2	5.4	5.9	5.1
Benzophenone	2-300	0.997	5189.9 ± 115.8	33444.7	1.0	11.4	1.5	7.1
2-Nitronaphthalene	2-300	0.994	4085.1 ± 134.8	38943.0	1.0	4.2	2.2	9.0
Biphenyl	0.1-60	0.998	21987.8 ± 353.2	4565.5	0.04	13.8[d]	5.9[d]	4.9[d]
Fluorene	0.2-300	0.994	11552.5 ± 330.1	99015.1	0.2	1.8	9.5	2.2
Phenanthrene	1-600	0.998	23467.6 ± 391.0	231577.4	0.2	15.1	5.1	5.2
Anthracene	1-300	0.999	10109.0 ± 126.2	37866.9	0.5	3.5	8.9	2.7

[a] Conditions: temperature: 60°C; MIL mass, 20 mg; extraction time, 60 min; stir rate: 400 rpm; NaCl concentration in aqueous solution, 30% (w/v).
[b] Standard deviation of regression.
[c] Precision at 2.5, 10, and 150 μg L^{-1}.
[d] Precision at 1, 4, and 120 μg L^{-1}.

$[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL resulted in higher enrichment factors for α,α,α-6-tetrafluoro-m-toluidine, 2-bromo-4-fluorobenzaldehyde, 1-chloro-4-nitrobenzene, biphenyl, and fluorene in comparison to the DLLME method. However, the DLLME method provided higher enrichment factors for the other seven analytes. The developed DLLME method permits a much faster extraction (2 minutes) while providing higher enrichment for many of the target analytes compared to the HS-SDME method (extraction time of 60 min). Additionally, temperature control is not required for the DLLME method. On the other hand, the developed SDME method maintains an advantage when sampling from complex matrices as the MIL microdroplet never comes in direct contact with the sample solution. Compared to other

Table 3. Enrichment factors of the target analytes using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL in the DLLME and the SDME methods.

Analyte	Enrichment Factor[a]			
	DLLME		SDME	
	$[P_{6,6,6,14}^{+}]_2$ $[MnCl_4^{2-}]$	$[Aliquat^{+}]_2$ $[MnCl_4^{2-}]$	$[P_{6,6,6,14}^{+}]_2$ $[MnCl_4^{2-}]$	$[Aliquat^{+}]_2$ $[MnCl_4^{2-}]$
Acetophenone	29.4	4.2	25.3	18.4
2-Chloroaniline	87.0	19.0	17.0	10.4
α,α,α-6-Tetrafluoro-m-toluidine	36.7	19.1	72.7	71.1
2-Bromo-4-fluorobenzaldehyde	36.3	10.0	46.0	42.4
1-Chloro-4-nitrobenzene	36.8	14.8	45.8	38.6
4-Chlorobutyrophenone	38.1	20.4	24.9	14.1
Benzophenone	41.2	27.5	32.4	19.5
2-Nitronaphthalene	36.0	29.2	29.1	16.1
Biphenyl	46.4	29.8	82.1	78.2
Fluorene	44.6	31.5	58.0	24.1
Phenanthrene	55.6	31.1	49.4	8.2
Anthracene	64.3	37.2	21.8	1.7

[a] Calculated at 30 μg L^{-1} for α,α,α-6-tetrafluoro-m-toluidine, 12 μg L^{-1} for biphenyl, and 60 μg L^{-1} for all other analytes.

microextraction techniques, the developed MIL-HS-SDME method exhibits advantages such as the ability to use higher volume of extraction solvent and elimination of a desorption step, as shown in Table A2. This further highlights the applicability of MILs in sample preparation techniques.

2.3.4. Analysis of real samples

Following the optimization and validation of the DLLME and the HS-SDME methods with the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL, the analysis of a real lake water sample was performed. The NaCl content of the real sample was adjusted to 30% (w/v) based on the previously described experimental results. No analytes were detected in the unadulterated lake water sample. Table 4 shows the relative recoveries and the reproducibility obtained using both methods at 20 μg $L^{-1}$and 100 μg L^{-1} (n=3). The relative recoveries for the DLLME method ranged from 68.7%

Table 4. Relative recoveries of the target analytes from lake water using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL by the optimized DLLME and SDME method.

Analyte	% Recovery ± SD (n=3)			
	DLLME		SDME	
	20 μg L^{-1}	100 μg L^{-1}	20 μg L^{-1}	100 μg L^{-1}
Acetophenone	104.5 ± 8.5	77.0 ± 3.6	76.8 ± 9.3	70.4 ± 7.4
2-Chloroaniline	68.7 ± 13.8	86.3 ± 3.7	82.0 ± 7.7	78.1 ± 7.2
α,α,α-6-Tetrafluoro-m-toluidine[a]	77.0 ± 7.1	72.7 ± 6.7	109.6 ± 3.6	69.2 ± 3.6
2-Bromo-4-fluorobenzaldehyde	79.2 ± 4.3	108.2 ± 13.2	89.2 ± 10.7	76.7 ± 10.8
1-Chloro-4-nitrobenzene	85.1 ± 6.3	85.8 ± 9.1	88.8 ± 3.3	66.8 ± 12.4
4-Chlorobutyrophenone	82.7 ± 10.9	77.1 ± 8.2	74.4 ± 14.0	85.4 ± 8.3
Benzophenone	71.5 ± 10.2	101.1 ± 6.5	83.4 ± 7.1	93.7 ± 6.7
2-Nitronaphthalene	91.7 ± 1.8	91.0 ± 10.2	93.0 ± 5.0	109.2 ± 10.3
Biphenyl[b]	87.3 ± 12.2	79.5 ±3.1	70.2 ± 4.3	87.2 ± 8.5
Fluorene	101.8 ± 3.0	89.6 ± 2.6	72.3 ± 11.2	105.7 ± 3.8
Phenanthrene	83.6 ± 3.8	80.1 ± 10.8	83.6 ± 13.6	75.2 ± 5.3
Anthracene	72.7 ± 13.7	76.5 ± 8.3	78.6 ± 4.6	86.7 ± 14.9

[a] Recovery at 10 and 50 μg L^{-1}.
[b] Recovery at 4 and 20 μg L^{-1}.

to 104.5% at 20 μg L^{-1} and from 72.7% to 108.2% at 100 μg L^{-1}. The relative recovery values varied from 70.2% to 109.6% at 20 μg L^{-1} and from 66.8% to 109.2% at 100 μg L^{-1} for the HS- SDME method. Relatively low recovery values were observed for some analytes using both methods, which can be explained by matrix effect. The standard deviation values for the recoveries were at or below 14.9%. These results demonstrate that the developed methods exhibited good reproducibility and sensitivity when applied to real world samples.

2.4 Conclusions

Two hydrophobic, tetrachloromanganate-based MILs were successfully applied for the first time as extraction solvents in HS-SDME coupled to HPLC. The magnetic susceptibility of the MILs imparted high stability to the microdroplet permitting sampling under elevated temperatures and long extraction times. Following extraction, the analyte-enriched droplet was

directly subjected to HPLC analysis. The optimized HS-SDME method was directly compared to the DLLME method employing the same two MILs as extraction solvents. The DLLME method provided much faster extraction time and higher enrichment for analytes with low vapor pressure, whereas HS-SDME showed advantages in extracting analytes possessing relatively high vapor pressure. Both methods exhibited low LODs and high precision for the target analytes as well as acceptable relative recoveries from a lake water sample, indicating that the examined MILs can be successfully applied in microextraction techniques. The total sampling time required of the DLLME method was less than 5 minutes, which demonstrates its potential as a high throughput sampling technique. Longer sampling time was necessary for the HS-SDME method. However, the HS-SDME method can be easily employed in cases of complex matrices since it is not necessary for the extraction solvent to be subjected to the sample solution.

The use of $[MnCl_4^{2-}]$-based MILs provides tremendous advantages over the conventional DLLME and HS-SDME methods as they provide more convenient ways to perform extractions. Also, the low UV absorbance of the $[MnCl_4^{2-}]$-based MILs permits the direct coupling to HPLC for chromatographic analysis. Furthermore, the selectivity of the extraction solvent can be varied by altering the substituent groups on the cationic component. These advantages provide attractive features when using MILs for the two microextraction techniques examined in this study, particularly in the development of high throughput and automated methods that can be compatible with complex matrices.

Acknowledgements

The authors acknowledge funding from the Chemical Measurement and Imaging Program at the National Science Foundation (Grant number CHE-1413199).

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CHAPTER 3

DETERMINATION OF UV FILTERS IN HIGH IONIC STRENGTH SAMPLE SOLUTIONS USING MATRIX-COMPATIBLE COATINGS FOR SOLID-PHASE MICROEXTRACTION

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Jiwoo An, Jared L. Anderson

Abstract

A double-confined polymeric ionic liquid (PIL) sorbent coating was fabricated for the determination of nine ultraviolet (UV) filters in sample solutions containing high salt content by direct immersion solid-phase microextraction (DI-SPME) coupled to high-performance liquid chromatography (HPLC). The IL monomer and crosslinker cations and anions, namely, 1-vinyl-3-decylimidazolium styrenesulfonate ([VImC_{10}][SS]) and 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([$(VBIm)_2C_{12}$] 2[SS]), were co-polymerized to create a highly stable sorbent coating which allowed for up to 120 direct-immersion extractions in 25% NaCl (w/v) solution without a decrease in its extraction capability. Extraction and desorption parameters such as desorption solvent, agitation rate, extraction time, desorption solvent volume, and desorption time were evaluated and optimized. The analytical performance of the styrenesulfonate anion-based PIL fiber, PIL fiber containing chloride anions, and a commercially available polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber were compared. Coefficients of determination (R^2) for the styrenesulfonate anion-based PIL fiber ranged from 0.995 to 0.999 and the limits of detection (LODs) varied from 0.1 to 5 μg L^{-1}. The developed method was successfully applied in real

water samples including tap, pool, and lake water, and acceptable relative recovery values were obtained. The lifetime of the PIL fiber containing chloride anions as well as the PDMS/DVB fiber were considerably shorter than the PIL fiber containing the styrenesulfonate anion, with both fibers showing a notable decrease in reproducibility and significant damage to the sorbent coating surface after 40 and 70 extractions, respectively. The R^2 values for the chloride anion containing PIL fiber were at or higher than 0.991 with LODs ranging from 0.5 to 5 μg L^{-1}. For the PDMS/DVB fiber, R^2 values ranged from 0.992 to 0.999 and LODs were found to be as low as 0.2 μg L^{-1} and as high as 5 μg L^{-1}.

3.1 Introduction

Personal care products (PCPs) refer to a wide range of substances including cosmetics, disinfectants, and plasticizers that are used in everyday lives [1, 2]. Ultraviolet (UV) filters are a well-known class of ingredients found in cosmetic products such as sunscreens, lotions, and lip- sticks, as well as plastics, adhesives, and paints [3, 4]. A combination of UV filters is added to the aforementioned products to protect skin from two types of solar radiation (UV-A and UV-B) [3, 5] or to prevent UV degradation of materials [4]. Studies have indicated that UV filters can accumulate directly or indirectly in environmental water sources from recreational activities (sea, lake, swimming pool) or industrial discharge [5]. However, many compounds belonging to the UV filter family are now considered emerging contaminants due to their ecotoxicity and possible endocrine disrupting characteristics [6, 7].

In an attempt to monitor and control the level of UV filters in water sources, a number of analytical methods have been developed over the past decade focusing on the detection of these compounds in the environment. As the trend in analytical chemistry moves towards

miniaturized and automated sampling processes [8], many newly introduced methods for the detection of UV filters are based on microextraction techniques. Liquid-phase microextraction (LPME) is among the most widely-used methods for the extraction of UV filters and includes single-drop microextraction (SDME) [6, 9], hollow fiber liquid phase microextraction (HF-LPME) [10], stir bar dispersive liquid microextraction (SBDLME) [11] and conventional or ultrasound-assisted dispersive liquid-liquid microextraction (DLLME or UA-DLLME, respectively) [12–15]. The aforementioned LPME methods employ various solvents to preconcentrate the target UV filters from water samples. Organic solvents such as tetrachloroethylene and chloroform are common extraction solvents for DLLME methods, and often these methods require disperser solvent volumes up to 1 mL to successfully perform the extraction.

Sorbent-based microextraction techniques that further reduce the use of organic solvents are an alternative to LPME. Several sorbent-based microextraction techniques have been reported for UV filter monitoring, such as solid-phase microextraction (SPME) [3, 4, 16] and stir bar sorptive-dispersive microextraction (SBSDME) [17]. These methods have utilized polymerized sorbent materials or magnetic nanoparticles (MNPs) as an extraction phase. Ionic liquids (ILs) and deep eutectic solvents (DESs) are widely utilized as alternative solvents in various LPME techniques in order to reduce toxic organic waste [18]. ILs are a non-molecular class of solvents with melting points at or below 100 °C [19]. Their physicochemical characteristics such as low vapor pressure, variable solvent miscibility, viscosity, and high stability have resulted in the application of various ILs as extraction solvents in a few reported LPME studies regarding UV filters [6, 9–11, 20]. Unlike LPME methods, the use of IL-based sorbents has not been explored in SPME for the determination of UV filters. Polymeric ionic

liquids (PILs) not only possess physicochemical characteristics inherent to ILs, but they can also be incorporated as sorbent coatings for SPME [21]. The tunability of ILs allows for the structural modification of PIL sorbent coatings for selective analyte extractions as well as for a specific mode of analysis (i.e., headspace or direct-immersion) [21]. PIL-based sorbent coatings have been applied in SPME for the determination of a wide variety of analytes including polycyclic aromatic hydrocarbons (PAHs) [22, 23], fatty-acid methyl esters (FAMEs) [24], phthalate esters (PAEs) [25], and amines [26, 27]. However, the possibility of anion exchange has often been considered as a major drawback for PIL-based sorbent coatings when performing direct-immersion sampling from very complex sample matrices. As the counteranion within the PIL is not chemically bound, anion exchange can occur between the PIL sorbent coating and the sample matrix, ultimately changing the chemical properties of the sorbent material. [26]. For this reason, headspace extraction mode (HS-SPME) has most often been employed when using PIL-based fibers [28]. However, the use of HS-SPME is limited when extracting large molecules and when the method is paired with high-performance liquid chromatography (HPLC).

In 2012, a double-confined IL polymer was introduced by Qiu et al. where ILs containing polymerizable anions, namely, p-styrenesulfonate and 2-acrylamido-2-methylpropane sulfonic acid (AMPS), were utilized to copolymerize the cation and the counteranion onto the silica surface for multi-mode chromatography [29]. Shortly thereafter, a double-confined PIL-based SPME sorbent coating was reported [28]. Similar to the previous work, the p-styrenesulfonate counteranion was copolymerized along with the IL cation onto a stainless-steel surface to create a robust and stable sorbent coating material [28]. In comparison to the same IL containing the bromide counteranion, it was proven not only that the

copolymerized fiber exhibited no anion exchange capabilities, but it could also be used in sample solutions containing high salt content using the direct immersion (DI-SPME) mode. More recently, the p-styrenesulfonate anion has been applied in monolith SPME [30] and hollow fiber SPME (HF-SPME) [31] for the analysis of endocrine disrupting chemicals from aqueous samples and estrogens from milk samples, respectively. This type of copolymerized PIL-based sorbent coating can overcome the ion-exchange tendency that PIL coatings inherently face, expanding the types of sample matrices in which these coatings can be used.

In this work, an IL monomer and crosslinker, namely, 1-vinyl-3-decylimidazolium styrenesulfonate ([VImC_{10}][SS]) and 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([(VBIm)$_2C_{12}$] 2[SS]), are reported for the first time as double-confined PIL-based SPME sorbent coatings for the extraction of 9 UV filters in high ionic strength sample solutions using DI-SPME. Unlike the previously reported studies where only the IL monomer was utilized to create double-confined PIL fibers, this study utilized both the IL monomer and crosslinker to fabricate the sorbent coating. In addition, fibers with significantly thicker films were constructed using a highly reproducible, reliable, and consistent photo-initiated polymerization process. The copolymerization of monomer and crosslinker cations and anions yielded a fiber with extended lifetime compared to other PIL-based and commercial SPME fibers when used in sample solutions with high salt concentration. The developed SPME method was coupled to HPLC with UV detection. The analytical performance of the copolymerized PIL-based fiber was compared with another PIL-based fiber containing the chloride counteranion and a commercially available polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber. This method demonstrates that the copolymerized PIL-based fiber can be

successfully applied in DI-SPME for the extraction of various UV filters in a sample solution containing high ionic strength.

3.2 Experimental

3.2.1 Materials and reagents

Oxybenzone (BP3) (98.0%), benzyl-salicylate (BS) (≥99.0%), 2-ethylhexyl 4-methoxycinnamate (EMC) (98.0%), 2-ethylhexyl 4-(dimethylamino)benzoate (EPP) (98.0%), 2-ethylhexyl salicylate (ES) (≥99.0%), etocrylene (ETO) (98.0%), octocrylene (OCR) (≥98.0%), homosalate (HS) (≥99.0%), avobenzone (BMDM) (≥99.0%), acrylonitrile (99.0%), 1,12-dibromododecane (98.0%), 1-vinylimidazole (≥99.0%), 1-chlorodecane (98.0%), vinyltrimethoxysilane (VTMS) (98.0%), and 2-hydroxy-2-methylpropiophenone (DAROCUR 1173) (>96.0%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Acetonitrile, acetone, methanol, ethyl acetate, and isopropanol with purities equal to or higher than 99.0% were also purchased from Sigma Aldrich. Lithium bis[(trifluoromethyl)sulfonyl]imide ($LiNTf_2$) was purchased from SynQuest Laboratories (Alachua, FL, USA). Sodium chloride and hydrogen peroxide (30.0%, w/w) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Sodium p-styrenesulfonate hydrate (>93.0%) was purchased from Tokyo Chemical Industries (Tokyo, Japan). Nitinol wire (128 μm in diameter) was purchased from Nitinol Devices & Components (Fremont, CA, USA). All solutions were prepared with ultrapure water (18.2 MΩcm) produced by a Milli-Q water filtration system (Millipore, Bedford, MA, USA). PDMS and PDMS/DVB fibers were obtained from Supelco (Bellefonte, PA, USA).

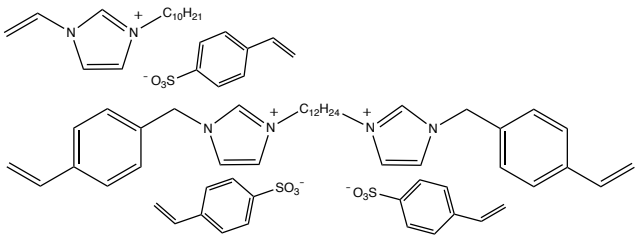
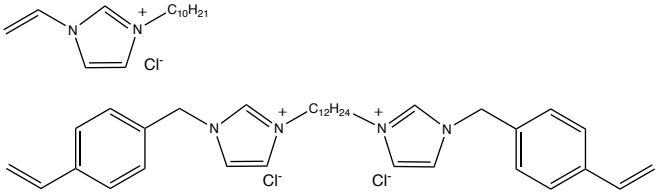
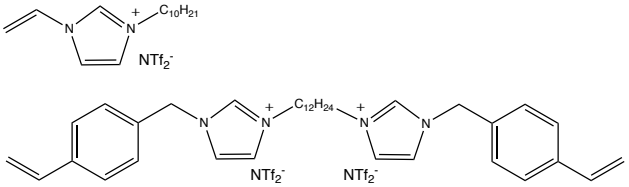
Individual stock solutions of the nine analytes were prepared at 5000 mg L^{-1} in methanol, with exception of EPP, ES, and BMDM, which were prepared at 1000 mg L^{-1}. A

working solution containing all nine analytes was prepared at 200 mg L^{-1} in methanol. The sample solution was prepared fresh by spiking an appropriate amount of stock solution into ultrapure water or a 25% NaCl (w/v) aqueous solution. The amount of organic solvent in aqueous sample solution was kept at 0.1% (v/v) at all times.

3.2.2 Synthesis of polymeric ionic liquids (PILs)

A total of six different monomers and crosslinkers were synthesized for PIL sorbent coatings, as shown in Table 1. The ILs 1-vinyl-3-decylimidazolium chloride ([$VImC_{10}$][Cl]), 1-vinyl-3-decylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([$VImC_{10}$][NTf_2]), 1,12-di(3-vinylbenzylimidazolium) dodecane dichloride ([$(VBIm)_2C_{12}$] 2[Cl]) and 1,12-di(3-vinylbenzylimidazolium)dodecane dibis[(trifluoromethyl)sulfonyl]imide ([$(VBIm)_2C_{12}$] 2[NTf_2]) were synthesized according to previously published procedures [22,32,33]. The preparation of 1-vinyl-3-decylimidazoliumstyrenesulfonate([$VImC_{10}$][SS])was carried out in a similar manner to a previously reported method [28] by mixing [$VImC_{12}$][Cl] with an aqueous solution of sodium p-styrenesulfonate at 1:1.1M ratio. The solution was stirred overnight at room temperature in darkness. Afterwards, the product was extracted with ethyl acetate (5mL × 5) and washed with ultrapure water. An aqueous silver nitrate (1 M) solution was used to test the existence of [Cl^-] in the aqueous phase. Ethyl acetate was removed by rotary evaporation and the product dried under vacuum. The crosslinker 1,12-di(3-vinylbenzylimidazolium) dodecane distyrenesulfonate ([$(VBIm)_2C_{12}$] 2[SS]) was synthesized by the same method as the monomer using a molar ratio of 1:2.1 of [$(VBIm)_2C_{12}$] 2[Cl] and the aqueous solution of sodium p-styrenesulfonate, respectively. The ^{1}H NMR spectral data for all monomers and crosslinkers used in the study are shown in Figs. B1-B6 (Appendix B).

Table 1. Structures and approximate film thickness of all fibers employed in this study.

	Structure	Approximate film thickness (μm)
Fiber **1**		83[a]
Fiber **2**		148[a]
Fiber **3**		128[a]
Fiber **4**	PDMS	100
Fiber **5**	PDMS/DVB	60

[a] Sorbent coating thickness was measured and estimated by SEM imaging.

2.3. Fiber fabrication

Modification of the nitinol fibers was performed according to previously published studies [21,34,35]. A mixture of ILs comprised of monomer and crosslinker (50% weight of the monomer) was homogenized and DAROCUR 1173 was added. The amount of DAROCUR 1173 was kept at 5% of the IL mixture (w/w) for styrenesulfonate-based PIL fibers and at 3% for all other PIL fibers. The coating mixture was placed on a hotplate under low heat, and 1 μL of methanol was added to promote homogenization. The mixture was coated onto the modified nitinol surface and the coated fibers were placed in the UV chamber for 2 h.

2.4. Instrumentation

Synthesized ILs were characterized by collecting ^{1}H NMR spectra in deuterated dimethyl sulfoxide using a Bruker DRX 500MHz nuclear magnetic resonance (NMR) spectrometer (Billerica, MA, USA). A RPR-100UV reactor purchased from Southern New England Ultraviolet Company (Bradford, CT, USA) was used for UV-initiated polymerization of PILs. UV lamps with a wavelength of 360 nm were used for [NTf_2^-] based PILs whereas 254 nm was used for [SS^-] and [Cl^-] based PILs. The film thickness of PIL based fibers were studied with FEI Quanta-250 scanning electron microscope (SEM).

Chromatographic separations were performed with a Shimadzu LC-20A HPLC system (Tokyo, Japan) consisting of a manual injector, a DGU-20A_3 degasser, two LC-20AT pumps, and a SPD-20 UV/Vis detector. All separations were carried out using a Restek Ultra II C18 column (250 mm × 4.6 mm, 5.0 μm, State College, PA, USA). Ultrapure water and acetonitrile (mobile phase A and B, respectively) were utilized as mobile phases for the separation of all compounds. A gradient separation was started with 80% B and increased to 100% in 3min, followed by a 10 min isocratic hold. Detection of all analytes was achieved at 310 nm except for BMDM, which was monitored at 254 nm. A representative chromatogram after the extraction using Fiber 1 is shown in Fig. B7.

An Agilent 1260 Infinity HPLC with a binary pump and a diode array detector (DAD) coupled to an Agilent 6230B Accurate Mass Time of Flight (TOF) mass spectrometer with an electrospray ion (ESI) source (Santa Clara, CA, USA) was used for LC-MS analysis. Separation of analytes was carried out using a Restek Ultra II C18 column (250 mm × 4.6 mm, 5.0 μm) prior to MS analysis. Conditions of ESI-MS were as follows: nebulizing gas, 35 psi;

drying gas (N_2) flow rate, 9 L min^{-1}; drying gas temperature, 350 °C; capillary voltage, 3500 V; spectra scan rate, 1 spectrum s^{-1}.

2.5. Optimization

Parameters including desorption solvent, agitation, extraction time, desorption solvent volume, and desorption time were investigated. The desorption solvent parameter was first optimized for all 5 fibers employed in this study as it was shown in the previous study to have low dependency on other parameters [35]. Salt concentration optimization was performed only with Fiber 1, and the remaining parameters were optimized for both Fiber 1 and the PDMS/DVB fiber. Fiber cleaning time was investigated to ensure fast and efficient cleaning of the fibers post-extraction.

2.6. Solid-phase microextraction procedure

All fibers were pre-conditioned in ultrapure water for 2 min prior to extraction. An aliquot of 10 mL of ultrapure water or 25% NaCl solution (w/v) was placed in a 10 mL amber vial, and the sample solution was stirred for 1min to promote pre-equilibration. DI-SPME was performed by subjecting the fiber directly into the sample solution for 60 min (commercial fibers) or 75 min (PIL fibers) at room temperature. A small magnetic stir bar was added and the sample solution was stirred at a constant stir rate of 900 rpm (commercial fibers) or 700 rpm (PIL fibers). Following extraction, the fiber was exposed to the optimal volume of desorption solvent for 10 min (PIL fibers) or 15 min (commercial fibers). Then, 20 μL of the desorption solvent was subjected to HPLC. The fiber was washed in ultrapure water for 2 min to remove any salt adsorbed onto the sorbent coating surface, followed by a 5 min wash in methanol.

2.7. Method validation

The analytical parameters including linear range, limits of detection (LODs), and relative recovery were determined using the Fiber 1, Fiber 2, and the PDMS/DVB fiber. A calibration curve containing a minimum of five concentration levels was constructed for each analyte. The LODs were determined at a signal-to-noise ratio of 3 (S/N=3). Tap water was collected after running the tap for 5 min. Pool water was collected from a local outdoor swimming pool (Ames, IA, USA). Lake water was collected from Oak Grove Beach (Johnston, IA, USA) and was used as a real sample to evaluate relative recovery. The collected lake water was passed through nylon filters (0.45μm) before extraction. For all water samples, NaCl was added to make an aqueous salt solution containing 25% NaCl (w/v).

3.3 Results and discussion

3.3.1 Sorbent coating selection for procedure optimization

The three PIL-based fibers examined in this study are composed of the same cationic structures but with different anions (Table 1). PIL-based fibers containing [NTf_2^-] or [Cl^-] anions have been utilized in several studies for the extraction of polar and non-polar analytes [22, 27, 32, 35]. PILs containing the styrenesulfonate anion have been applied in techniques such as HF-SPME [31] and SPME [28, 30] coupled to HPLC and GC, though they have not been studied extensively in microextraction techniques to date. Fiber 1 reported in this study contains the styrenesulfonate as a counteranion in both IL monomer and crosslinker and possesses a higher ratio of aromatic moieties compared to the other commonly used PIL sorbent coatings (i.e., Fibers 2 and 3). Furthermore, copolymerization of the anion results in a fiber with higher stability, mainly overcoming unwanted anion exchange between the matrix

component and the fiber sorbent coating, as reported in a previous study [28]. Among the many factors that affect extraction efficiencies, the addition of salts to the analytical sample can often increase extraction efficiencies in SPME through the salting out effect [36]. However, addition of salt is generally discouraged in DI-SPME mode as the salt or other matrix components cause the fiber coatings to be easily damaged, thus reducing the fiber lifetime [36]. Employment of double-confined fibers can overcome this inherent weakness and expand the class of matrices in which DI-SPME can be performed. In order to explore the stability and performance of the styrenesulfonate anion within the sorbent coating in sample solutions containing high ionic strength, one PIL-based fiber (Fiber 1) and one commercially available fiber (PDMS/DVB) were selected for optimization. Subsequently, the analytical performance of Fiber 1, Fiber 2, and the PDMS/DVB fiber were evaluated and compared.

3.3.2 Optimization of extraction and desorption parameters

3.3.2.1 Desorption solvent optimization

The desorption solvent was optimized individually for all five fibers. Fig. B8 (a-e) shows the effectiveness of methanol, acetonitrile, and acetone when used as desorption solvents for each fiber. Methanol and acetone resulted in comparable peak areas for most analytes using Fiber 1 and the PDMS/DVB fiber (Fig. B8a and B8d, respectively). However, BMDM was not detected when acetone was used as desorption solvent with the PDMS/DVB fiber (Fig. B8d). Considering these results, methanol was chosen as the optimal desorption solvent for Fiber 1 and the PDMS/DVB fiber. As for the remaining PIL-based fibers (Fibers 2 and 3), the highest peak areas were observed for most of the analytes using acetone as desorption solvent (Fig. B8b and B8c). The PDMS fiber exhibited the most dissimilar results

compared to the other fibers with acetonitrile being the optimal desorption solvent for all 9 analytes (Fig. B8e).

3.3.2.2 Extraction/desorption optimization using Fiber **1**

Extraction and desorption parameters including salt concentration, sample agitation rate, extraction time, desorption volume, and desorption time were examined using a factor-by-factor method. To examine the effects of ionic strength in the extraction of UV-filters using Fiber 1, a series of extractions were performed in aqueous sample solutions containing 0%, 10%, and 25% NaCl (w/v). As shown in Fig. 1, an increase in the ionic strength of the sample solution increased the peak areas of all analytes. Addition of NaCl to the sample solution was especially favorable for the extraction of ETO and BP3, showing a sharp rise in peak areas as the salt concentration increased from 0% to 10% NaCl (w/v) and again from 10% to 25% NaCl (w/v). Though the maximum peak areas were observed for all analytes when 25% NaCl (w/v) sample solution was used, the effect of ionic strength was much less pronounced for BMDM,

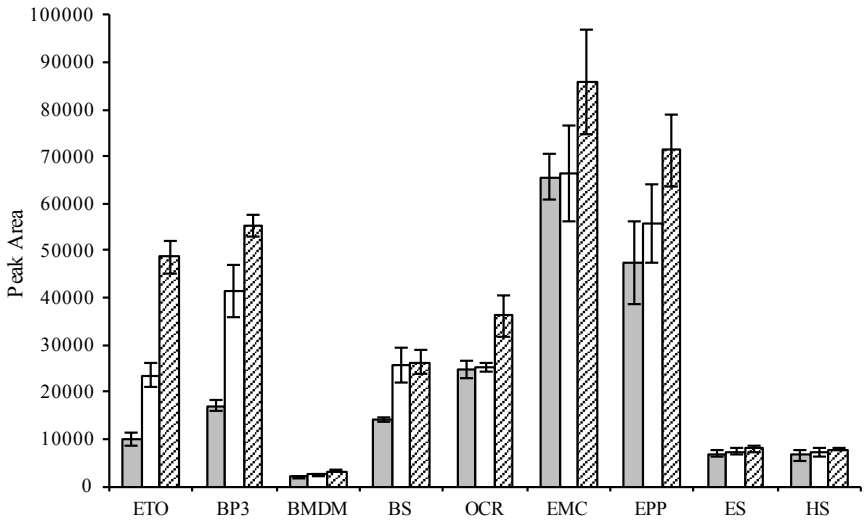


Figure 1. Comparison of extraction efficiencies based on peak area using Fiber **1** at different NaCl concentrations: (▩) 0% NaCl, (□) 10 % NaCl, and (▨) 25% NaCl (w/v). Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; extraction time: 30 min; stir rate: 500 rpm; desorption solvent: methanol; desorption time: 15 min; desorption volume: 40 μL.

ES, and HS. Therefore, an aqueous sample solution of 25% NaCl (w/v) was used for all subsequent experiments.

Performing the extraction under proper agitation conditions can not only accelerate diffusion of analytes from the sample to fiber coating, but it can also affect the equilibration time of the extraction system [37]. A total of 4 different agitation rates ranging from 300 to 900rpm were tested using Fiber 1. Increased peak areas were observed for all analytes as the stir rate increased up to 700rpm, as shown in Fig. B9a. Further enhancements in the stir rate to 900rpm resulted in comparable peak areas to 700rpm. However, the relative standard deviation (%RSD) values increased from 4.2% to 11.2% at 700rpm to 8.2% - 16.5% at 900 rpm. Consequently, 700 rpm was chosen as the optimal stirring rate for the PIL fibers.

Even though SPME is a non-exhaustive extraction method [38], obtaining quantitative and precise results is possible when sampling is performed under non-equilibrium conditions [37]. Though many methods may shorten the sampling time in order to increase sample throughput, maximum sensitivity is usually achieved when the extraction system has attained equilibration [39]. The extraction time was varied from 0 to 90 min to generate a sorption-time profile using Fiber 1, as shown in Fig. 2a. A steady increase in peak areas was observed up to an extraction time of 20 min with a relatively steep increase being observed from 60 to 75 min. No significant difference was observed when the extraction time was further increased to 90 min, indicating that the equilibrium was reached for the target analytes by 75 min.
Therefore, an extraction time of 75 min was used for all subsequent experiments.

A challenge in liquid desorption procedures is determining the minimum amount of solvent that can desorb the highest amount of target analytes, as a large sample volume can lead to significant extracolumn dispersion during the separation process, causing peak

broadening [40]. Desorption volume was optimized by using 30, 40, and 50 µL of methanol. Fig. B10a shows that based on the peak areas observed, an increase in the desorption solvent volume resulted in a higher mass of extracted analyte. The analytes EMC and EPP were most influenced by the desorption solvent volume, showing a significant improvement in peak areas when the desorption volume increased from 40 to 50 µL. Given these results, 50 µL of methanol was applied as the desorption volume for the PIL-based fibers.

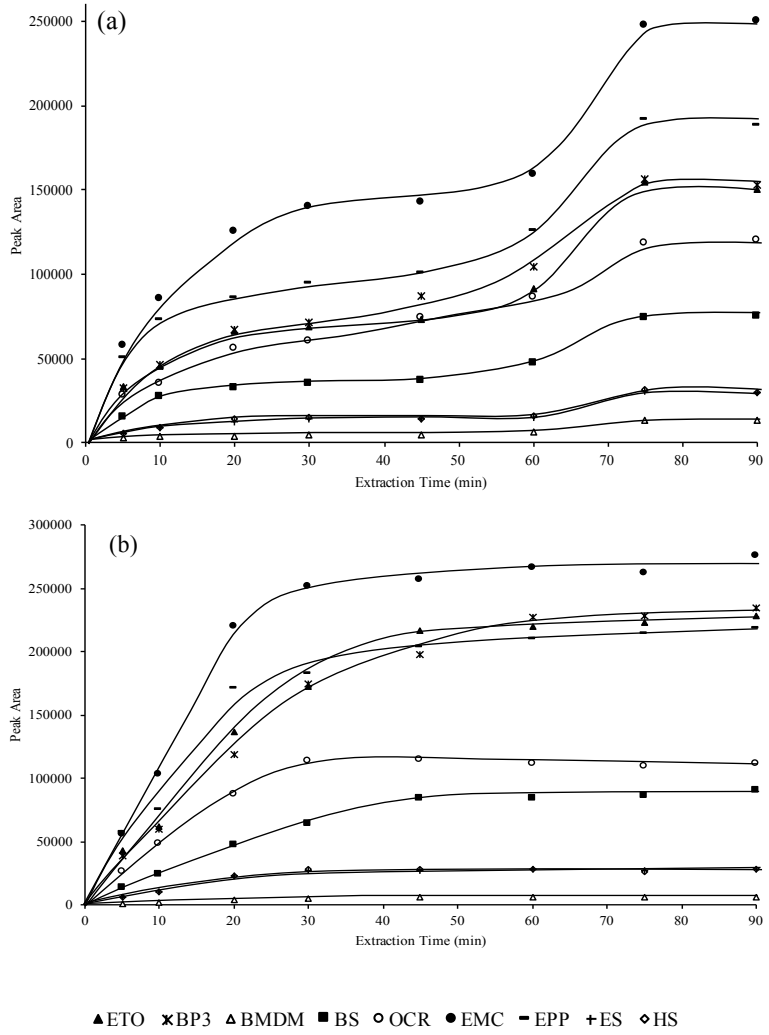


Figure 2. Sorption time profile of (a) Fiber **1** and (b) PDMS/DVB fiber. Experimental conditions (n = 3): analyte concentration: 200 µg L^{-1}; salt concentration: 25 % NaCl (w/v); stir rate: 700 rpm (Fiber 1) and 900 rpm (PDMS/DVB) rpm; desorption solvent: methanol; desorption time: 15 min; desorption volume: 40 µL.

Desorption time was optimized by performing static desorption in organic solvent for 5, 10, and 15 min Fig. B11a shows that static desorption at 5 min was not sufficient to desorb the target analytes from the fiber. When the time was increased to 10 min, a significant increase in extraction efficiency was observed for all analytes. However, no statistically substantial changes were observed when the desorption time was increased from 10 to 15 min. Based on these results, a desorption time of 10 min was chosen as the optimal parameter.

3.3.2.3 Extraction/desorption optimization using the PDMS/DVB fiber

The same extraction and desorption parameters were optimized for the PDMS/DVB fiber using a factor-by-factor method, with the exception of salt concentration. Unlike Fiber 1, a high agitation rate was beneficial for all analytes when extractions were performed using the PDMS/DVB fiber (Fig. B9b). A steep rise in extraction efficiency was observed from 700 to 900 rpm without a decrease in precision. Therefore, 900 rpm was selected as the optimal stir rate for the PDMS/DVB fiber. A sorption-time profile was also generated for the PDMS/DVB fiber using extraction times ranging from 0 to 90 min (Fig. 2b). The analytes BMDM, OCR, ES and HS reached a relatively fast equilibrium at around 30 min, whereas ETO, BP3, BS, EMC, and EPP required 45–60 min in order to attain equilibration. For maximum sensitivity of all analytes, 60 min was used as the extraction time for all subsequent experiments.

Fig. B10b shows the influence of desorption solvent volume for the PDMS/DVB fiber. In contrast to the results obtained with Fiber 1, a lower desorption solvent volume of 30 μL yielded higher peak areas for all analytes except EPP, which showed no significant difference between desorption solvent volumes of 30 and 40 μL. Moreover, longer desorption time was more effective for most of the analytes when the PDMS/ DVB fiber was used, as shown in Fig.

B11b. Considering these results for the PDMS/DVB fiber, 30 μL and 15 min were selected as optimal parameters for desorption solvent volume and time, respectively.

3.3.3 Assessment of analyte carryover

Carryover or memory effect is often not considered as a major concern in SPME unless the concentration of analytes is low where trace amounts of analytes sorbed on the fiber from a previous extraction can affect the equilibrium between the fiber coating and the sample solution [41]. Many studies that have coupled SPME to liquid chromatography perform multiple desorption steps or flush the desorption chamber in order to eliminate the carryover effect [42–44]. To minimize analyte carryover, the fiber cleaning time was optimized prior to evaluating the analytical performance of Fiber 1. After the initial desorption in 50 μL of methanol, the fiber was washed with methanol for 2, 3, and 5 min under stirring. The washed fiber was then immersed in 50 μL of fresh methanol for a second desorption step, and the desorption solvent subjected to HPLC analysis. As can be seen in Fig. B12, analyte carryover was greatly reduced by increasing the fiber wash time from 2 to 3 min. When the wash time was increased to 5 min, no peaks were detected for most of the analytes. Therefore, the fiber cleaning time was reduced from 20 min to 5 min for all subsequent analyses.

3.3.4 Fiber to fiber comparison of extraction efficiencies

Following the extraction of the target analytes using all 5 fibers employed in this study, the extraction efficiency of all fiber was estimated by two methods: direct comparison of peak areas of analytes and the normalized peak areas. The normalized peak areas were calculated by the ratio between peak areas and the approximate film thickness of each fiber measured by SEM (see Table 1). Fig. 3 shows the obtained results. The approximate film thickness of Fiber 1 was higher than the PDMS/DVB fiber, and similar peak areas were found for analytes such

as ETO and BP3 (Fig. 3a). Higher peak areas were observed for all other analytes using Fiber 1. These results are also demonstrated by the LODs, which show that similar or lower LOD values were obtained with Fiber 1 compared to the PDMS/DVB fiber for most analytes.

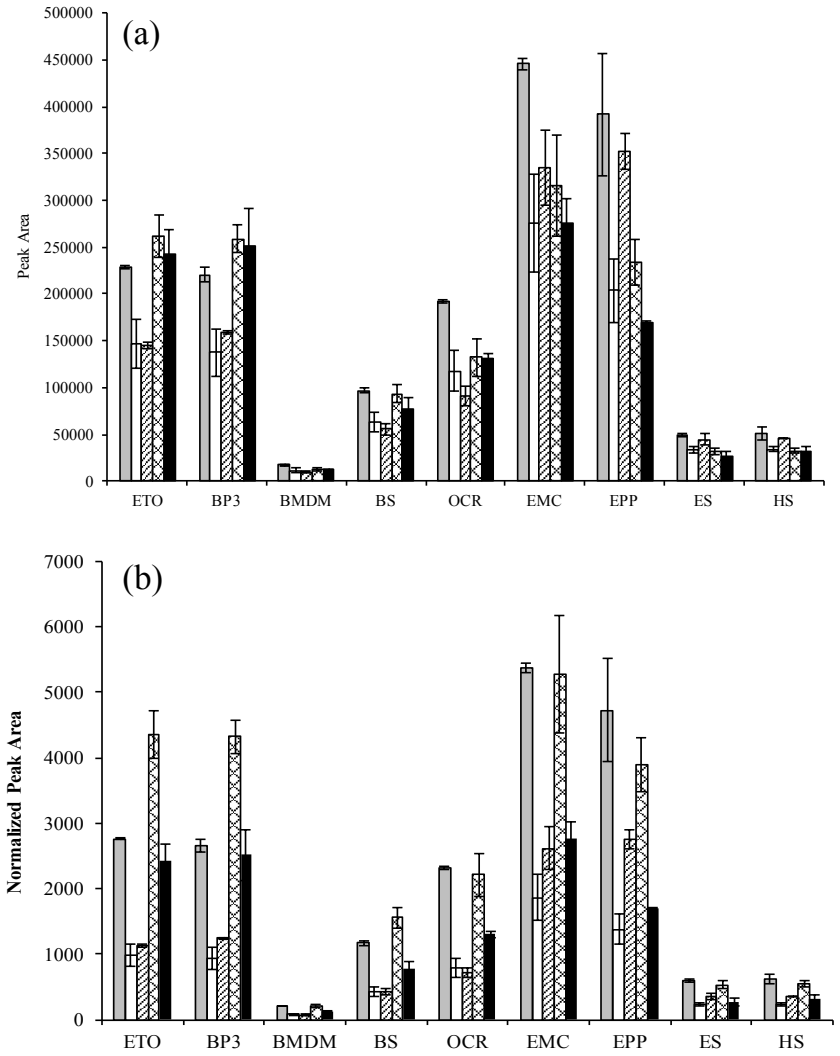


Figure 3. Comparison of peak areas after three replicate extraction/desorption cycles using all fibers (a) without normalization and (b) after normalization by the approximate film thickness of each fiber (see Table 1 for the approximate film thicknesses). (▒) Fiber **1**, (□) Fiber **2**, (▨) Fiber **3**, (▩) PDMS/DVB, and (■) PDMS fiber. Experimental conditions for Fibers 1, 2, and 3 (n=3): analyte concentration: 200 µg L^{-1}; salt concentration: 25 % NaCl (w/v); extraction time: 75 min; stir rate: 700 rpm; desorption solvent: methanol (Fiber 1) and acetone (Fibers 2 and 3); desorption time: 10 min; desorption volume: 50 µL. Experimental conditions for the PDMS and PDMS/DVB fibers (n=3): analyte concentration: 200 µg L^{-1}; salt concentration: 25 % NaCl (w/v); extraction time: 60 min; stir rate: 900 rpm; desorption solvent: methanol (PDMS/DVB) and acetonitrile (PDMS); desorption time: 15 min; desorption volume: 30 µL.

Normalized peak areas (Fig. 3b) show that the extraction efficiencies of the target analytes for Fiber 1 and the PDMS/DVB fiber are much more similar under the normalized condition, with exception of ETO and BP3. Additionally, Fiber 1 exhibited outstanding reproducibility compared to other fibers with %RSD values falling below 5.0%. Fibers 2 and 3 were the least favorable in the extraction of the target analytes. The PDMS fiber exhibited fair extraction capabilities of ETO and BP3. However, normalized peak areas for all other analytes were much lower than those of Fiber 1 and the PDMS/DVB fiber.

3.3.5 Detection of UV filters using HPLC-ESI-TOF

The detection of UV filters has most often been accomplished with gas chromatography (GC) [15], gas chromatography-mass spectrometry (GC-MS) [12–15, 17], gas chromatography-tandem mass spectrometry (GC-MS/MS) [3, 4], and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [45–47]. The use of LC coupled to time-of-flight (TOF) mass spectrometry with electrospray (ESI) ionization was considered for the detection of the target UV filters. Detailed LC-TOF instrumental parameters are included in Section 2.4. The same extraction procedure was carried out using Fiber 1 and the desorption solvent was diluted to 80μL for the injection using an autosampler. The injected sample was detected using a diode array detector (DAD) and subsequently analyzed by TOF-MS. As shown in Fig. B13, detection of the target analytes was proven to be difficult when TOF-MS was used in comparison to when DAD was used as a detection method. A relatively high extracted ion chromatogram (EIC) signal was obtained for BS and EPP compared to other analytes, whereas the analytes EMC and ES were not detected after the extraction was performed at 200 μg L^{-1}. Considering these results, HPLC with UV detection was employed for all subsequent analytical performance studies.

3.3.6 Analytical performance and recovery study

The analytical performance of Fiber 1, Fiber 2, and PDMS/DVB fiber was evaluated by carrying out extractions at a series of spiked concentration levels. All extractions for the analytical performance evaluation were completed in 25% aqueous NaCl solution (w/v). Table 2 lists the figures of merit for the 9 analytes extracted using Fiber 1, Fiber 2, and the PDMS/DVB fiber. Different linear ranges were obtained by constructing five- to seven-point calibration curves. Limits of detection (LODs) were acquired by decreasing the spiked analyte concentration until a signal-to-noise ratio of 3 (S/N=3) was achieved using UV detection. Correlation coefficient values (R^2) for Fiber 1 ranged from 0.995 to 0.999, and the LODs varied from 0.1 to 5 μg L^{-1}. Good reproducibility at the LODs was observed with the % RSD values ranging from 1.8% to 11.6%. For Fiber 2, R^2 values differed from 0.991 to 0.999, with LODs ranging from 0.5 to 5 μg L^{-1}. Values of %RSD at or below 13.9 were obtained at LODs. The PDMS/DVB fiber resulted in R^2 values varying from 0.992 to 0.999. Comparable LODs to Fiber 1 were acquired, with their values being as low as 0.2 μg L^{-1} and as high as 5 μg L^{-1}. Acceptable reproducibility was also obtained using the PDMS/DVB fiber with %RSD values at or below 10.4%.

To evaluate the applicability of the fibers in real samples, relative recoveries were assessed in water samples that may be likely to contain the target analytes. Three different water samples were tested including tap water, pool water, and lake water. The tap and pool water were collected and NaCl was added to make up a 25% aqueous NaCl solution (w/v). The salt was added to the lake water after the collected lake water sample was passed through 0.45 μm filters. No observable peaks were detected for most analytes except for EMC, which was detected below the LOD using Fiber 1 when the real samples were analyzed without analyte

Table 2. Figures of merit for the 9 analytes extracted using Fiber **1**, Fiber **2**, and the PDMS/DVB fiber.

Analyte	Acronym	Linear range (µg L $^{-1}$)			R^2			LOD (µg L $^{-1}$)			%RSD[c] (n=3)		
		Fiber **1**[a]	Fiber **2**[a]	PDMS/ DVB[b]	Fiber **1**[a]	Fiber **2**[a]	PDMS/ DVB[b]	Fiber **1**[a]	Fiber **2**[a]	PDMS/ DVB[b]	Fiber **1**[a]	Fiber **2**[a]	PDMS/ DVB[b]
Ethyl 2-cyano-3,3-diphenylacrylate	ETO	1-100	2-200	1-100	0.997	0.995	0.998	0.5	1	0.2	8.5	6.2	6.9
Oxybenzone	BP3	1-150	2-200	0.5-100	0.995	0.997	0.999	0.2	1	0.2	11.6	7.1	7.0
Avobenzone	BMDM	10-150	10-200	10-200	0.998	0.991	0.992	5	5	5	10.1	11.4	5.5
Benzyl-salicylate	BS	1-150	5-200	2-100	0.998	0.998	0.999	0.5	2	1	5.6	8.9	9.2
Octocrylene	OCR	1-150	2-100	2-100	0.999	0.999	0.999	0.5	1	1	7.1	13.9	5.6
2-Ethylhexyl 4-methoxycinnamate	EMC	0.2-100	1-100	0.5-100	0.998	0.998	0.998	0.1	0.5	0.2	7.7	10.7	9.8
2-Ethylhexyl 4-(dimethylamino) benzoate	EPP	0.5-100	2-100	1-100	0.998	0.997	0.993	0.2	1	0.5	4.5	7.4	10.4
2-Ethylhexyl-salicylate	ES	5-150	5-200	5-200	0.998	0.996	0.999	2	2	2	4.1	9.4	7.4
Homosalate	HS	5-150	5-200	5-200	0.995	0.999	0.997	2	2	2	1.8	4.6	7.9

[a] Experimental conditions: Salt concentration: 25% NaCl (w/v); Stir rate: 700 rpm; Extraction time: 75 min; Desorption solvent: methanol; Desorption volume: 50 µL; Desorption time: 10 min.

[b] Experimental conditions: Salt concentration: 25% NaCl (w/v); Stir rate: 900 rpm; Extraction time: 60 min; Desorption solvent: methanol; Desorption volume: 30 µL; Desorption time: 15 min.

[c] % Relative standard deviation calculated at LOD.

Table 3. Relative recoveries of the target analytes from real samples using Fiber **1**, Fiber **2**, and the PDMS/DVB fiber.

Analyte	% Relative recovery ± SD (n = 3)[a,b]								
	Fiber **1**			Fiber **2**			PDMS/DVB		
	Tap	Pool	Lake	Tap	Pool	Lake	Tap	Pool	Lake
ETO	106.4±3.7	86.8±4.0	109.0±7.4	76.4±1.5	86.7±3.4	89.9±5.8	100.3±6.9	122.7±9.3	120.5±16.1
BP3	98.3±4.8	111.4±6.1	118.5±16.9	109.6±2.6	102.8±11.3	112.6±15.2	97.7±3.4	110.3±9.6	103.5±15.0
BMDM	93.1±6.0	99.9±4.3	108.2±7.3	95.7±8.7	87.8±11.3	70.1±14.8	85.2±3.3	78.9±9.2	54.5±13.2
BS	94.2±9.8	87.2±2.7	84.9±9.3	111.0±6.9	99.3±6.8	95.2±11.0	97.5±7.6	89.1±12.3	112.2.±8.6
OCR	102.3±5.4	83.9±5.6	72.5±6.1	87.9±5.5	91.4±2.0	77.4±3.8	97.2±2.1	82.0±10.4	69.1±4.0
EMC	98.5±3.1	99.1±10.8	117.9±8.2	102.6±8.1	106.8±8.8	92.7±11.0	96.0±2.7	99.6±11.4	76.8±6.6
EPP	97.1±6.6	82.5±7.7	83.0±17.3	73.1±3.6	72.7±3.5	70.7±1.6	107.6±6.1	98.1±17.3	73.2±7.2
ES	97.5±5.8	82.2±5.7	66.6±15.0	89.5±3.2	79.3±3.0	74.4±7.3	101.7±7.4	107.8±16.9	68.3±10.8
HS	96.3±3.5	96.0±10.0	88.3±15.3	94.6±6.6	94.3±12.5	81.0±15.9	103.1±6.7	123.7±10.1	77.9±11.2

[a] Concentration of all analytes at 10 μg L^{-1}.

[b] All extractions performed in 25% NaCl sample solution (w/v) at optimal conditions.

spiking. Table 3 shows the relative recovery values and the standard deviation of the 9 UV filters from each water sample at 10 μg L^{-1} using Fiber 1, Fiber 2, and the PDMS/DVB fiber. For Fiber 1, the relative recovery of the target analytes from tap water ranged from 93.2% to 106.4%, whereas they varied from 82.2% to 111.4% from the pool water. Lake water recovery values were as low as 66.6% and as high as 118.5%. For Fiber 2, the average relative recovery values were found to range from 73.1% to 111.0% in tap water. Additionally, recovery from the pool water ranged from 72.7% to 106.8% and from 70.1% to 112.6% in lake water. For the PDMS/DVB fiber, a relative recovery of 85.2–107.6% was obtained from tap water, 78.9–123.7% from pool water, and 54.5–120.5% from lake water. Matrix effects were relatively more significant for Fiber 2 and the PDMS/ DVB fiber when the pool and the lake water were used as sample matrices.

Table B1 (Appendix B) shows a comparison of analytical performance obtained using Fiber 1 with other reported microextraction methods for the determination of UV filters coupled to HPLC with UV detection. The number of analytes used in the previously reported studies were equal to or less than six UV filters, whereas a total of nine UV filter compounds were determined using this method. The LOD values were comparable to those of the existing methods. The developed DI-SPME method utilized a sample solution containing the highest salt content, demonstrating the robustness of the PIL-based SPME sorbent coating and its possibility to be applied in other complex matrices.

Approximately 120 DI-SPME extractions were performed in 25% NaCl aqueous sample solution (w/v) using Fiber 1 without a loss of reproducibility or extraction efficiency. Fig. B14 shows a representative SEM image of the Fiber 1, Fiber 2, and Fiber 3 sorbent coatings. Fiber 2 was replaced after 40 extractions. The PDMS/DVB fiber was replaced after

approximately 70 extractions in the high salt sample solution using DI mode, due to observable damage to the fiber surface and a clear decrease in reproducibility. Overall, Fiber 1 exhibited acceptable relative recovery values with good precision from the real water samples, proving that the double-confined PIL-based fiber containing phenyl groups (and π−electron capability) within the crosslinker and anion possesses higher stability compared to other PIL-based fibers or commercially available fibers, while also not being prone to undergoing ion-exchange with matrix components.

3.4 Conclusions

In this work, a double-confined PIL-based sorbent coating composed of both IL monomer and crosslinker was successfully constructed using a UV-initiated polymerization process and was applied for the determination of nine UV filters in sample solutions containing high salt concentrations using DI-SPME coupled to HPLC. The analyte-enriched desorption solvent was directly injected to HPLC for the separation of analytes. When an aqueous solution containing NaCl (25%, w/v) was used as a sample matrix, Fiber 1 exhibited the best extraction efficiencies and highest stability compared to Fiber 2 and the PDMS/DVB fiber. Low parts-per-billion level LODs were achieved with good reproducibility, and the fibers were applied in three different real samples including tap, pool, and lake water for the evaluation of relative recovery.

The co-polymerization of IL cations and anions resulted in a robust sorbent coating compatible with high salt solutions, overcoming the inherent drawback of limited matrix choices for SPME when DI extraction mode is used. Fiber 1 was used for approximately 120 extraction/desorption cycles without a loss of extraction efficiency, exhibiting a much longer

lifetime compared to the PDMS/DVB fiber. The double-confined sorbent coatings such as Fiber 1 greatly expands the types of possible matrices for DI-SPME while providing the capability of structural tuning of the PIL. Future work with the double-confined sorbent coatings are focused on biological or environmental applications which require sampling from complex matrices.

Acknowledgments

The authors acknowledge funding from the Chemical Measurement and Imaging Program at the National Science Foundation (Grant number CHE-1709372).

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CHAPTER 4

GENERAL CONCLUSIONS

This thesis summarizes the application of ILs, specifically, MILs and PILs, in microextraction techniques. The ILs applied in the studies were structurally modified to overcome the inherent disadvantages of the conventional methods. The two developed methods were directly compatible with HPLC, allowing faster analysis of the target analytes.

Chapter 2 describes the development of a SDME procedure utilizing MILs as extraction solvents directly coupled to HPLC and a comparison of the developed method to DLLME. The use of MILs as extraction solvents in SDME led to higher droplet stability in comparison to conventional organic solvents and the results indicated that good extraction efficiencies of twelve aromatic compounds were obtained. The $[MnCl_4^{2-}]$-based MILs also allowed the direct analysis of analyte-enriched extraction phase with HPLC with UV detection without further sample cleanup step, proving the advantage of MILs as extraction phase for microextraction techniques.

Chapter 3 of this thesis describes a use of novel double-confined PIL as a sorbent coating in SPME coupled to HPLC for the extraction of UV filters. The IL monomer and crosslinker were both composed of polymerizable cations and anion, creating an extremely stable sorbent coating in sample solutions containing high salt concentration (25% NaCl, w/v). The double-confined PIL fiber exhibited a much longer lifetime (~120 extraction/desorption cycles) in comparison to the commercially available PDMS/DVB fiber (~70 extraction/desorption cycles) when extractions were performed in high salinity sample matrix. Successful extraction and analysis of nine UV filter compounds were performed using the

double-confined PIL fiber in combination with HPLC, demonstrating possibility of its future application in complex environmental or biological matrices.

APPENDIX A

SUPPLEMENTAL INFORMATION ACCOMPANYING CHAPTER 2

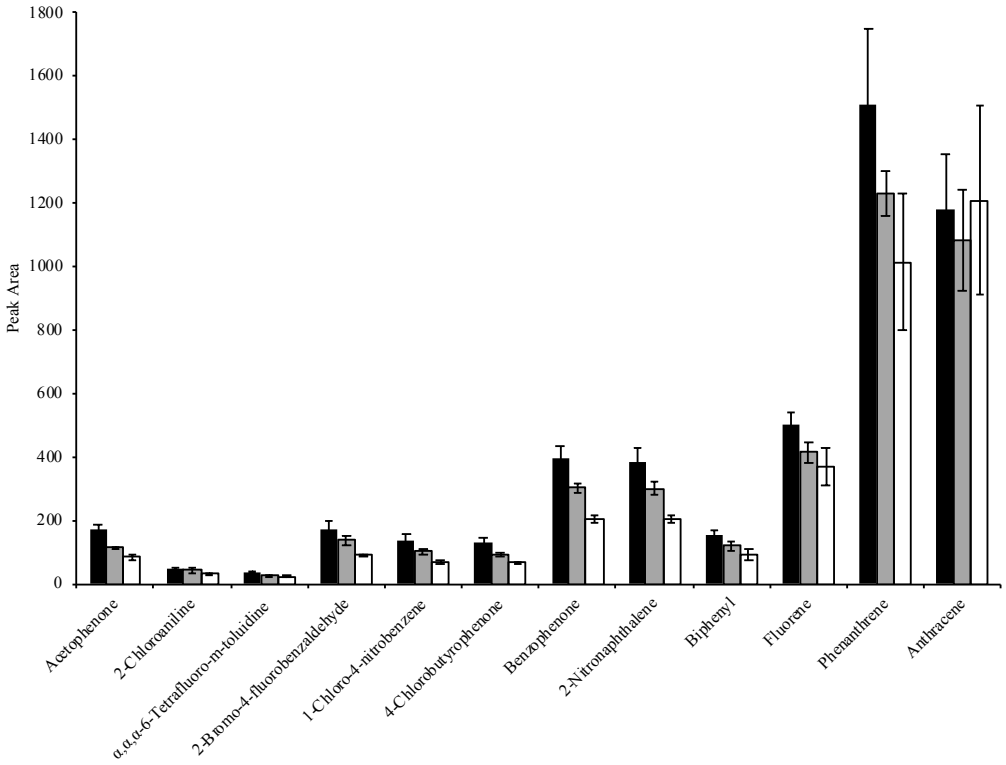


Figure A1. Comparison of the disperser solvent type for the DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL. Acetonitrile (black bar); methanol (gray bar); acetone (open bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; MIL mass: 20 mg; Disperser solvent volume: 5 μL; Extraction time: 30 s; NaCl concentration in the aqueous solution: 0% (w/v).

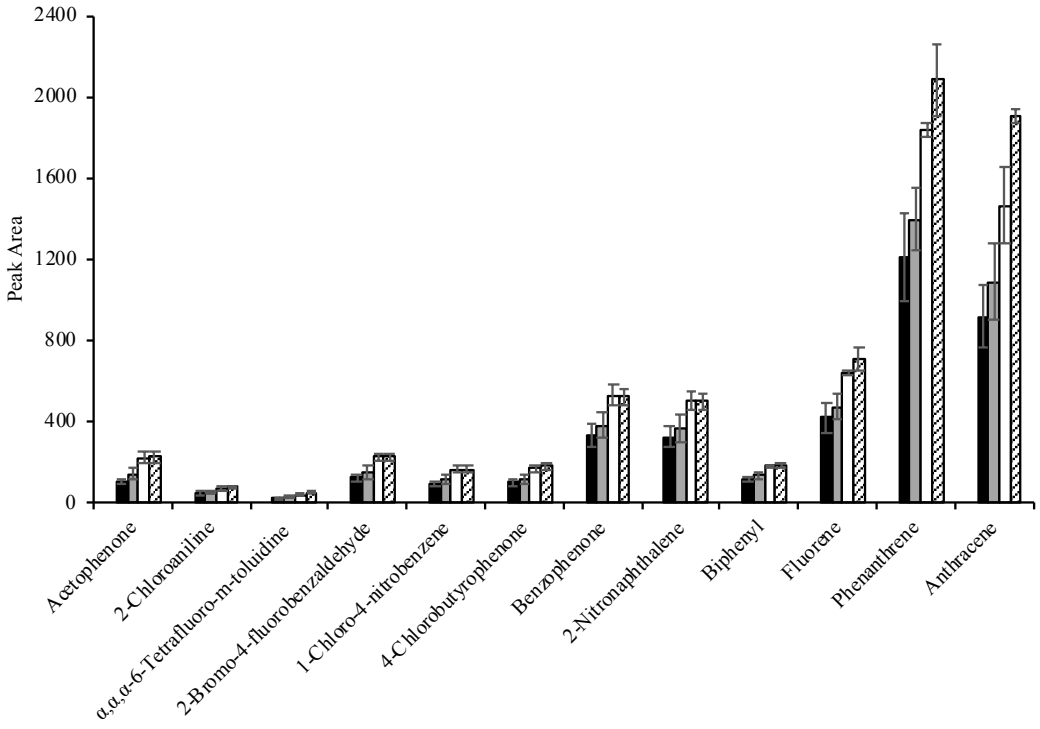


Figure A2. Comparison of the effect of MIL mass on the DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL. 5 mg (black bar); 10 mg (gray bar); 15 mg (open bar); 20 mg (dashed bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Disperser solvent: acetonitrile; Disperser solvent volume: 5 μL; Extraction time: 30 s; NaCl concentration in the aqueous solution: 0% (w/v).

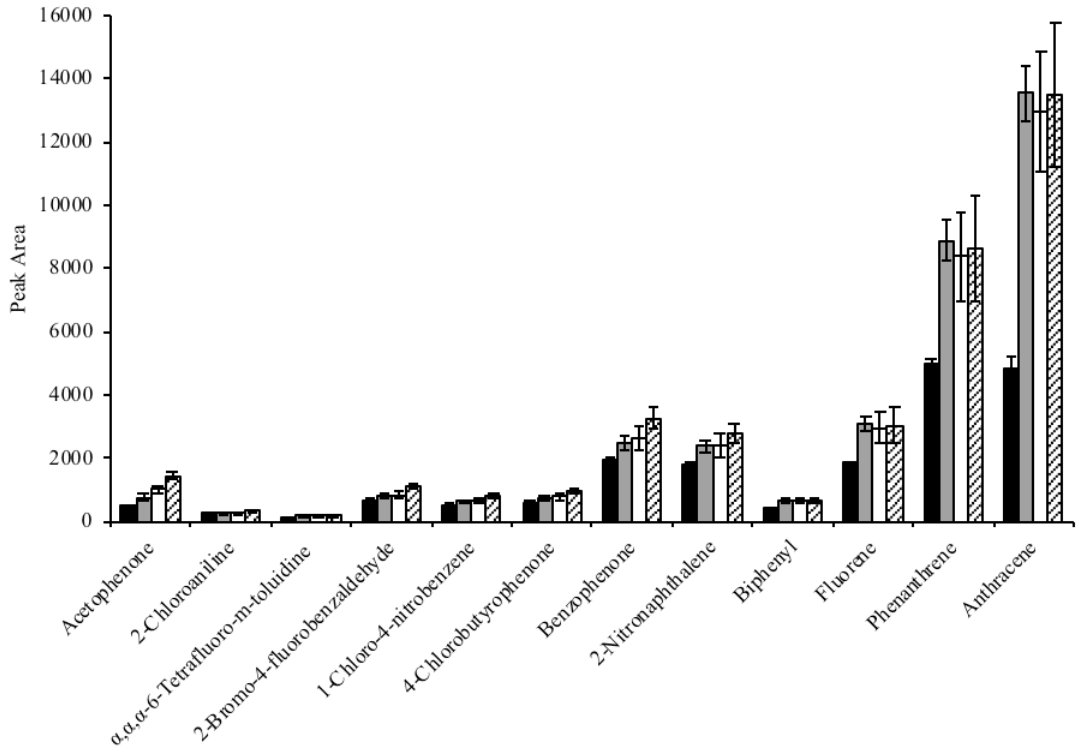


Figure A3. Effect of NaCl addition to the aqueous solution for DLLME method using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL. 0% (w/v) (black bar); 10% (w/v) (gray bar); 20% (w/v) (open bar); 30% (w/v) (dashed bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Disperser solvent: acetonitrile; MIL mass: 20 mg; Extraction time: 120 s; Disperser solvent volume: 20 μL.

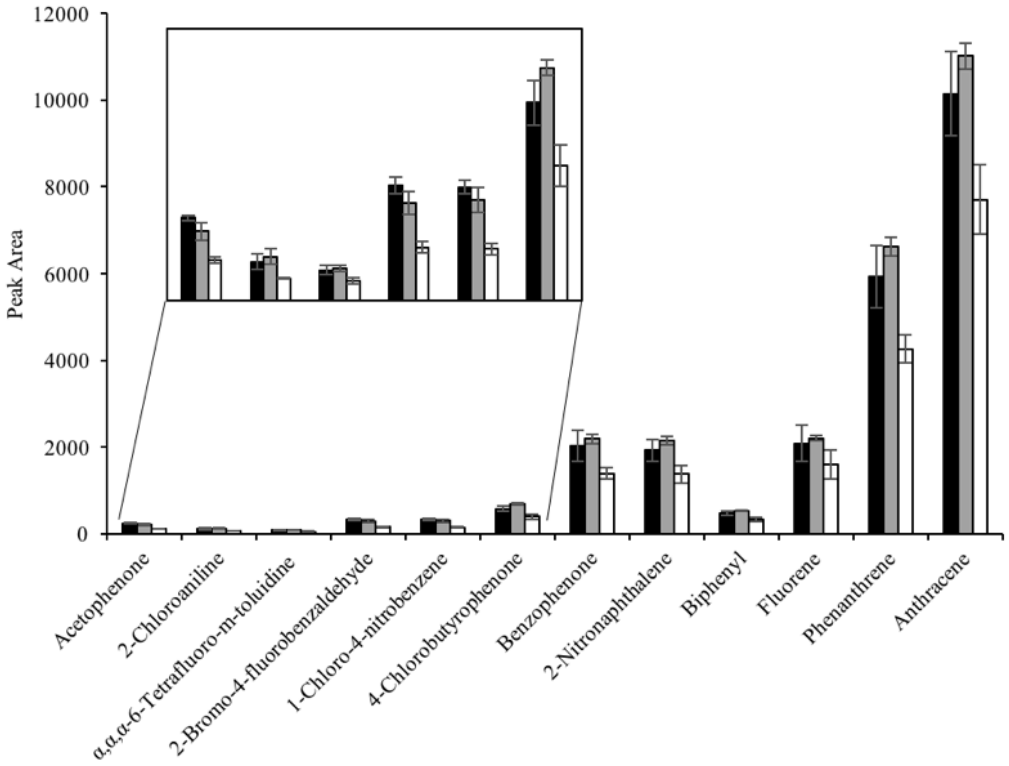


Figure A4. Comparison of the disperser solvent type for the DLLME method using the $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. Acetonitrile (black bar); methanol (gray bar); acetone (open bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; MIL mass: 20 mg; Disperser solvent volume: 5 μL; Extraction time: 30 s; NaCl concentration in the aqueous solution: 30% (w/v).

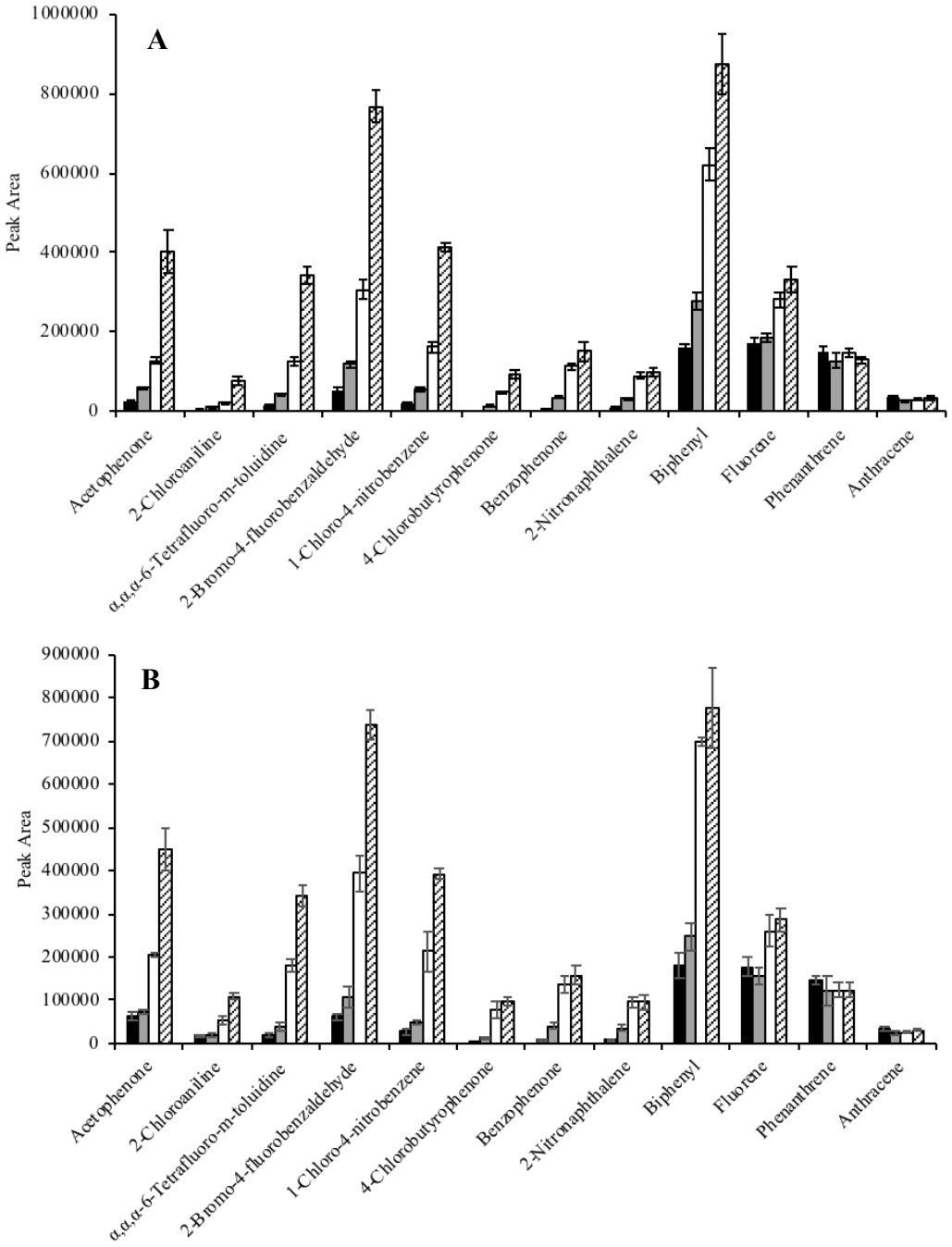


Figure A5. Effect of NaCl concentration in aqueous sample on extraction efficiencies for the SDME method using (A) $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and (B) $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. 0% NaCl (w/v) (black bar); 10% NaCl (w/v) (gray bar); 20% NaCl (w/v) (open bar); 30% NaCl (w/v) (dashed bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; Extraction time: 30 min; temperature: room temperature; MIL mass: 10 mg; stir rate: 800 rpm; headspace volume: 2.5 mL.

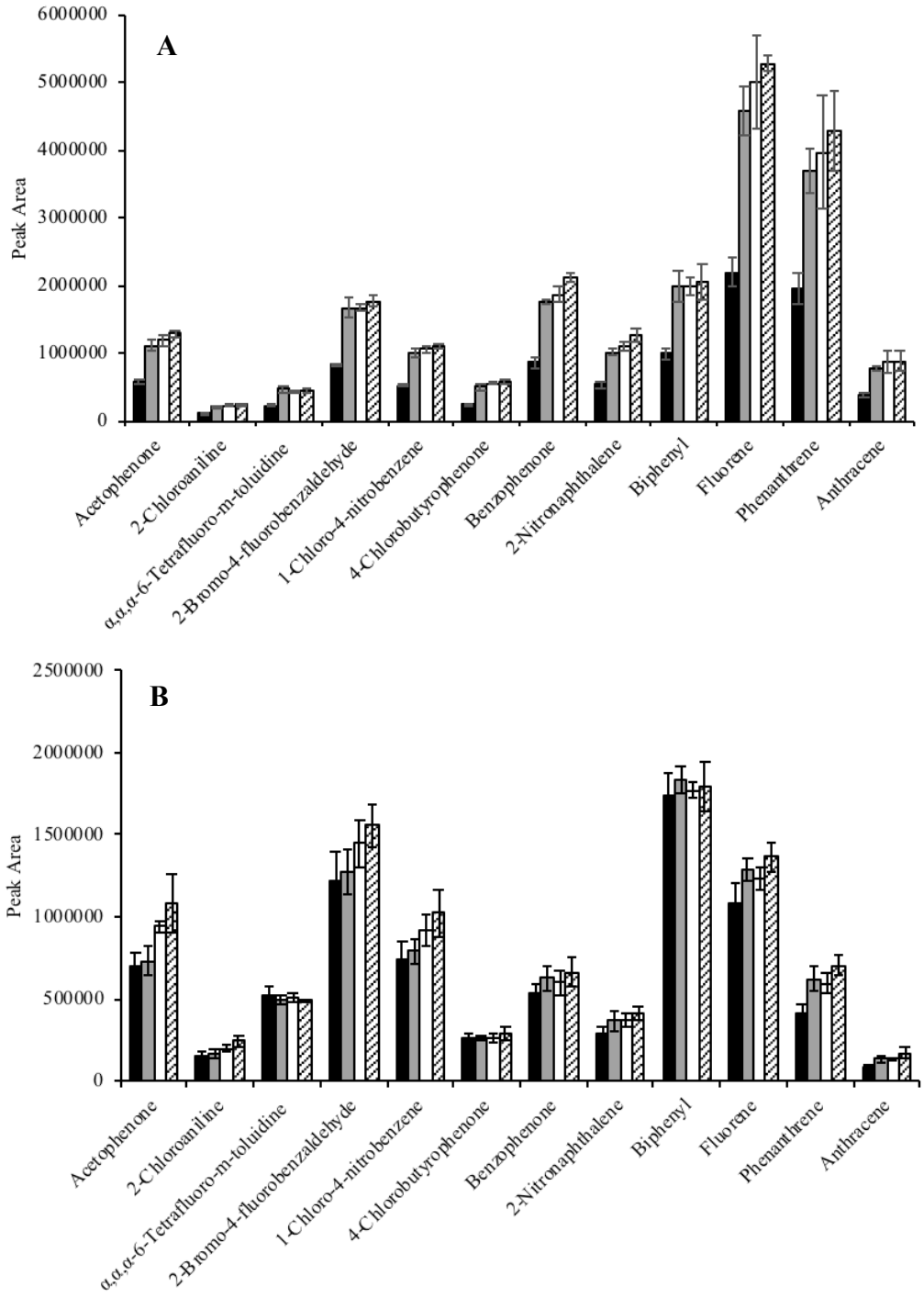


Figure A6. Effect of MIL mass on analyte extraction efficiencies for the SDME method using (A) $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and (B) $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. 5 mg (black bar); 10 mg (gray bar); 15 mg (open bar); 20 mg (dashed bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; NaCl concentration in the aqueous solution: 30% (w/v); Temperature: 60°C ($[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL) and 40°C ($[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL); Extraction time: 30 min; stir rate: 800 rpm; headspace volume: 2.5 mL.

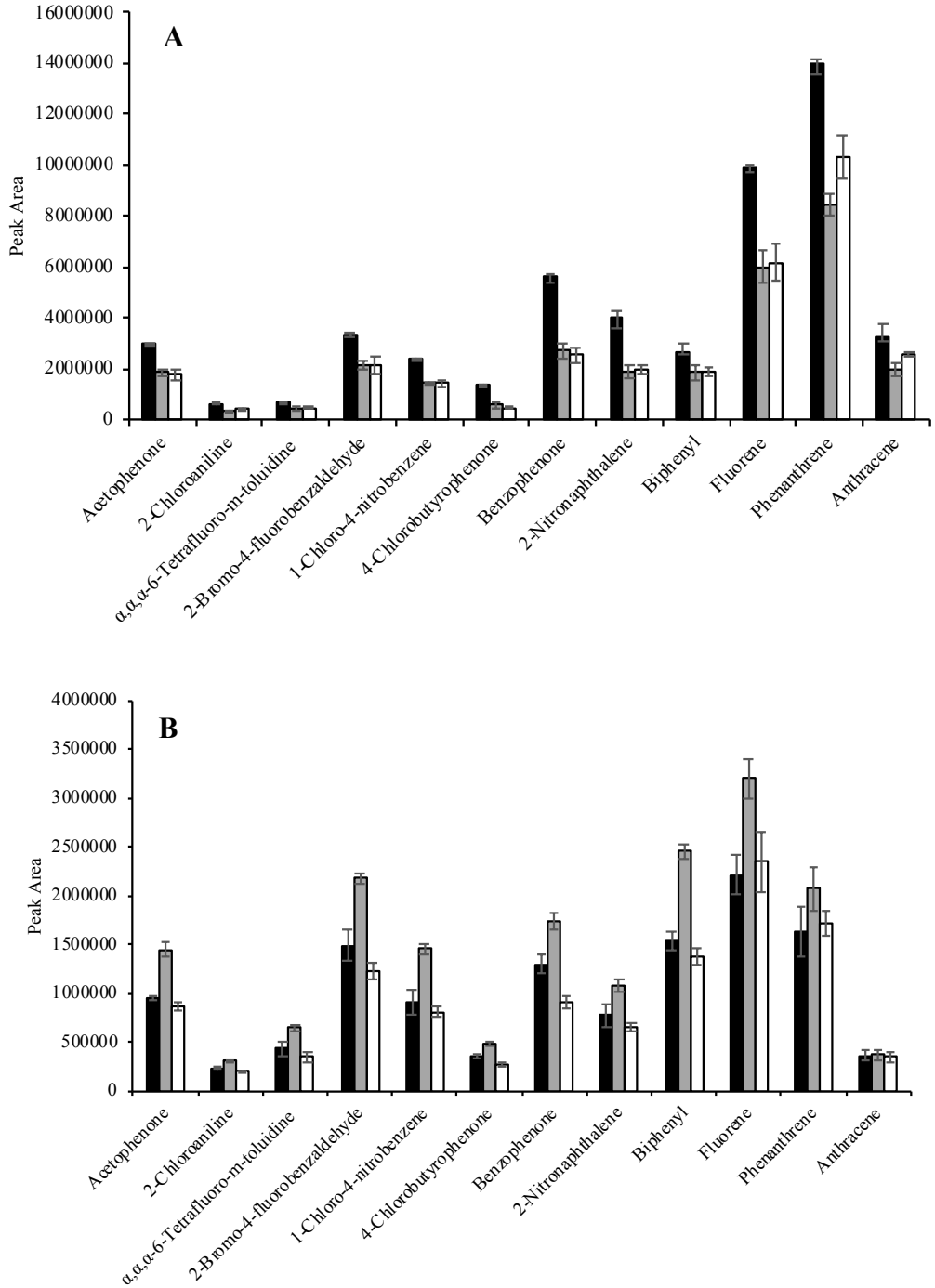


Figure A7. Effect of stir rates for the SDME method using (A) $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and (B) $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. 400 rpm (black bar); 800 rpm (gray bar); 1100 rpm (open bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; NaCl concentration in the aqueous solution: 30% (w/v); Temperature: 60°C ($[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL) and 40°C ($[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL); MIL mass: 20 mg; Extraction time: 60 min; headspace volume: 2.5 mL.

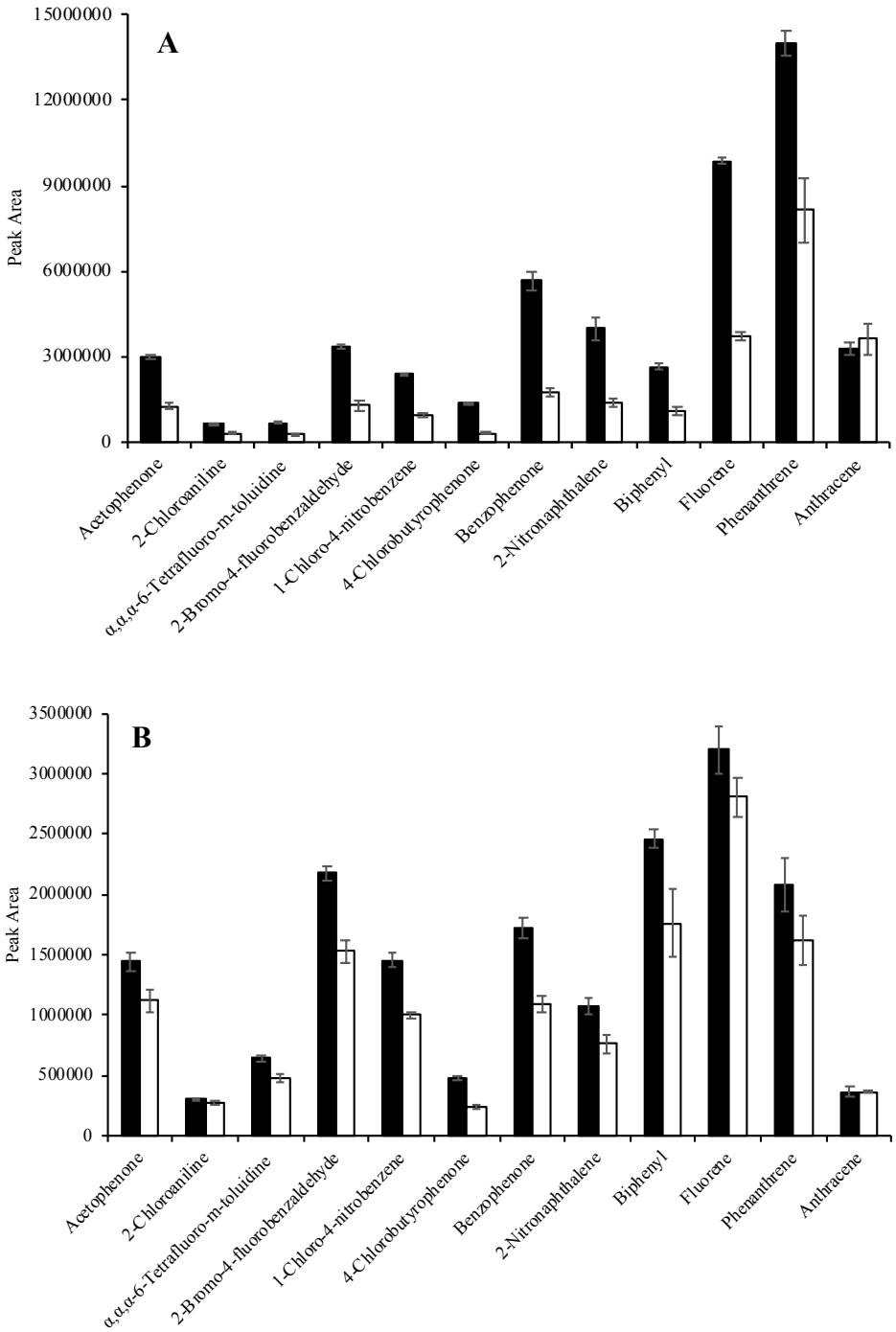


Figure A8. Effect of headspace volume for the SDME method using (A) $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL and (B) $[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL. 2.5 mL (black bar); 4 mL (open bar). Concentration of α,α,α-6-tetrafluoro-m-toluidine: 300 μg L^{-1}, concentration of biphenyl: 120 μg L^{-1}, concentration of all other analytes: 600 μg L^{-1}; NaCl concentration in the aqueous solution: 30% (w/v); Temperature: 60°C ($[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL) and 40°C ($[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL); MIL mass: 20 mg; Extraction time: 60 min; Stir rate: 400 rpm ($[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL) and 800 rpm ($[Aliquat^{+}]_2[MnCl_4^{2-}]$ MIL).

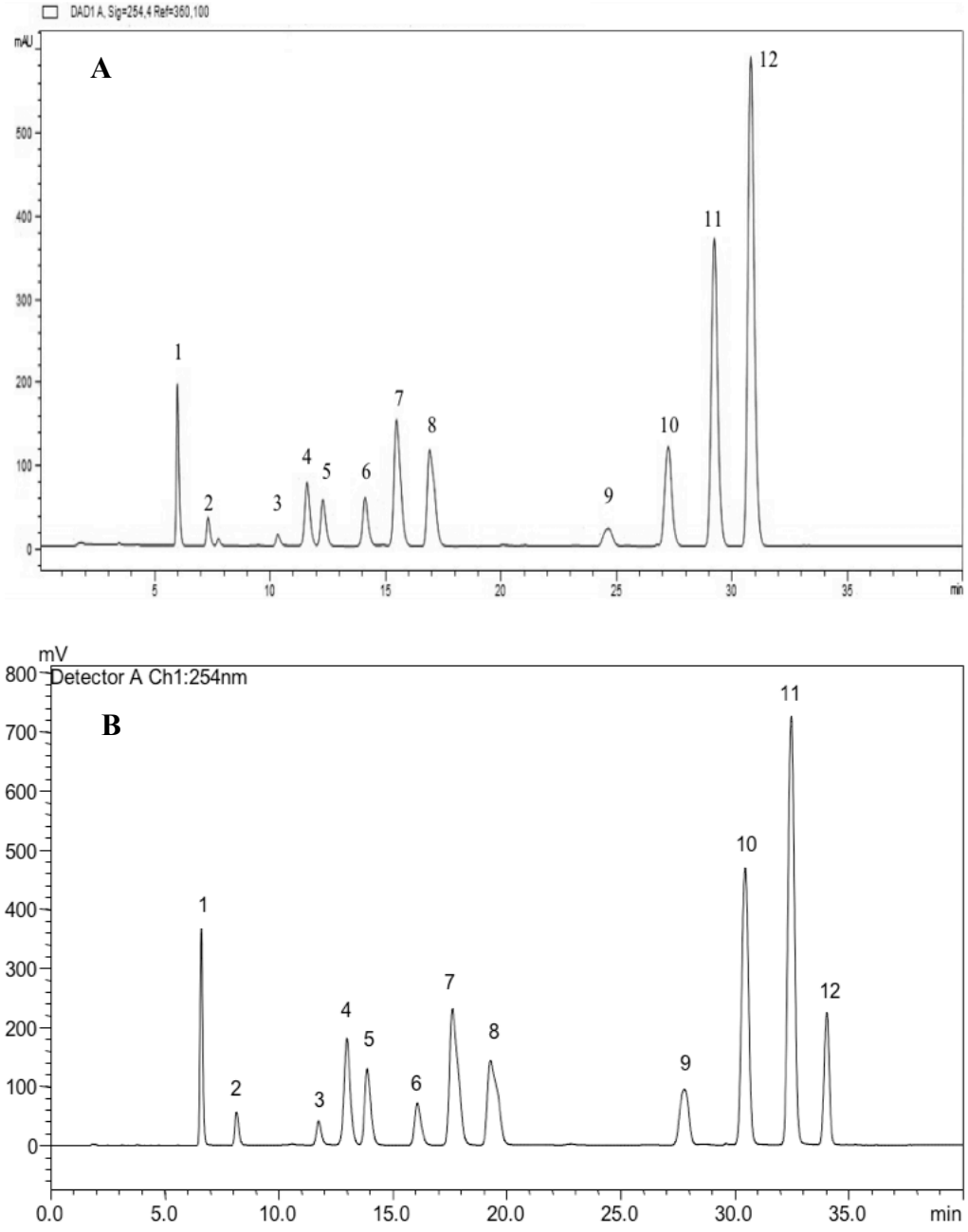
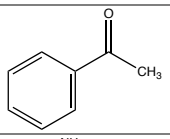
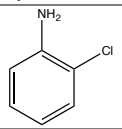
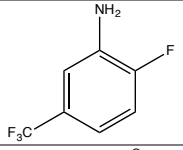
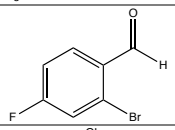
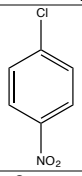
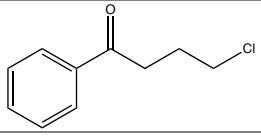
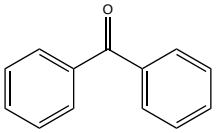
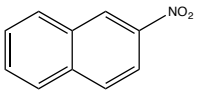
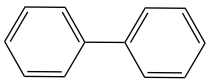
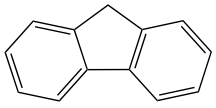
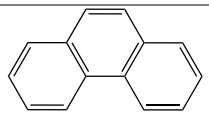
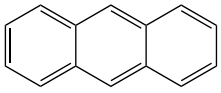


Figure A9. Chromatographic separation of enriched analytes at 0.6 µg mL^{-1} (0.3 µg mL^{-1} and 0.12 µg mL^{-1} for analytes 3 and 9, respectively) using the $[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ MIL by (A) DLLME and (B) HS-SDME method. (1) Acetophenone; (2) 2-chloroaniline; (3) α,α,α-6-tetrafluoro-m-toluidine; (4) 2-bromo-4-fluorobenzaldehyde; (5) 1-chloro-4-nitrobenzene; (6) 4-chlorobutyrophenone; (7) Benzophenone; (8) 2-nitronaphthalene; (9) Biphenyl; (10) Fluorene; (11) Phenanthrene; (12) Anthracene (The peak at 7.8 minutes in (A) originates from the impurity in the 2-chloroaniline standard).

Table A1. Structures and select properties of the analytes examined in the study.

Name	Structure	Log P [a]	Boiling Point [a] (°C)	Vapor Pressure [a] (Torr)
Acetophenone		1.60	202.0	0.299
2-Chloroaniline		2.01	208.8	0.209
α,α,α-6-Tetrafluoro-m-toluidine		2.64	172.1±40.0	1.35
2-Bromo-4-fluorobenzaldehyde		1.92	234.9±20.0	5.16×10^{-2}
1-Chloro-4-nitrobenzene		2.46	242.0	5.41×10^{-2}
4-Chlorobutyrophenone		2.53	285.9±23.0	2.72×10^{-3}
Benzophenone		3.21	305.4	8.23×10^{-4}
2-Nitronaphthalene		3.11	319.6±11.0	6.28×10^{-4}
Biphenyl		4.09	258.0±7.0	2.27×10^{-2}
Fluorene		4.32	293.6±10.0	3.00×10^{-3}
Phenanthrene		4.55	337.4±9.0	2.06×10^{-4}
Anthracene		4.55	337.4±9.0	2.06×10^{-4}

[a] Predicted values obtained from SciFinder.

Table A2. Comparison of developed MIL-HS-SDME parameters to other methods.

Method	Extraction solvent	Extraction solvent volume	Temperature (°C)	Detection method	Extraction time (min)	Other procedure	Reference
MIL-HS-SDME	$[P_{6,6,6,14}^{+}]_2[MnCl_4^{2-}]$ $[Aliquat^{+}]_2[MnCl_4^{2-}]$	20 mg[b]	60, 40	HPLC-UV	60	Direct injection	This study
HS-SPME	Polyaniline coating	50 μm	RT[c]	GC-FID	20[d]	Desorption required	[1]
HSME	1-Butanol	3 μL	40	GC-FID	12[d]	Desorption required	[2]
DI-SDME	[HMIM][FAP][a]	10 μL	RT	HPLC-UV	120	Direct injection	[3]

[a] 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
[b] Approximately 20 μL
[c] Room temperature
[d] Equilibrium not reached at indicated time

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APPENDIX B

SUPPLEMENTAL INFORMATION ACCOMPANYING CHAPTER 3

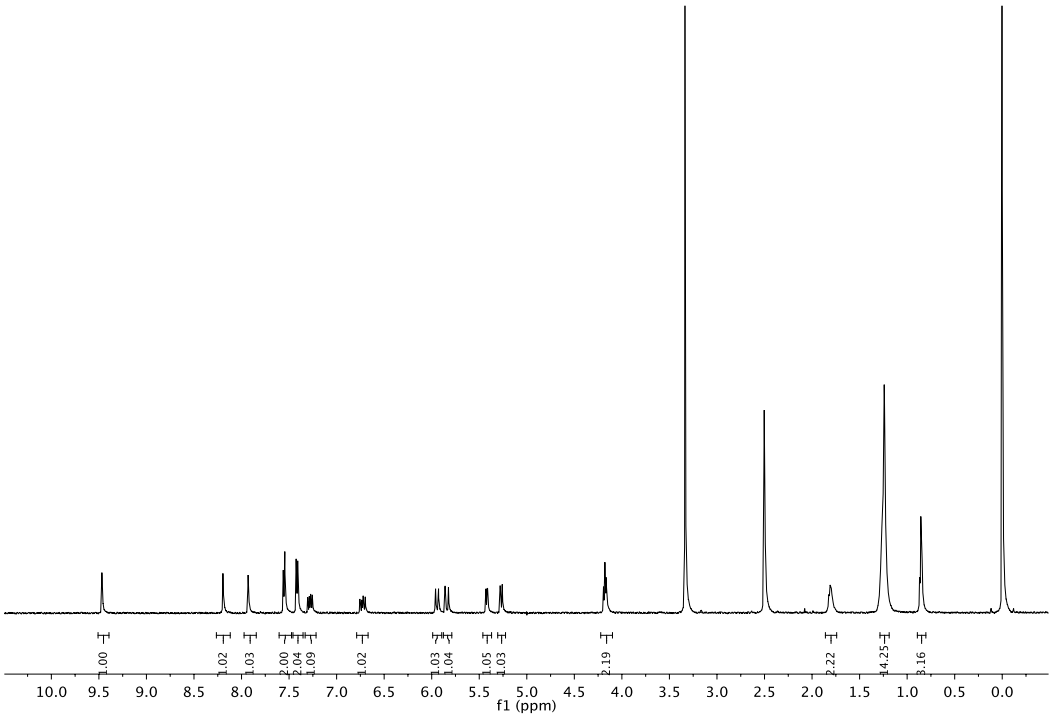

Figure B1. ^{1}H NMR spectrum of the [VImC_{10}][SS] monomer: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.47 (d, 1H), 8.20 (t, 1H), 7.93 (t, 1H), 7.60 – 7.47 (m, 2H), 7.42 (d, 2H), 7.28 (dd, 1H), 6.73 (dd, 1H), 5.95 (dd, 1H), 5.84 (dd, 1H), 5.42 (dd, 1H), 5.31 – 5.22 (m, 1H), 4.18 (t, 2H), 1.80 (d, 2H), 1.24 (s, 14H), 0.86 (t, 3H).

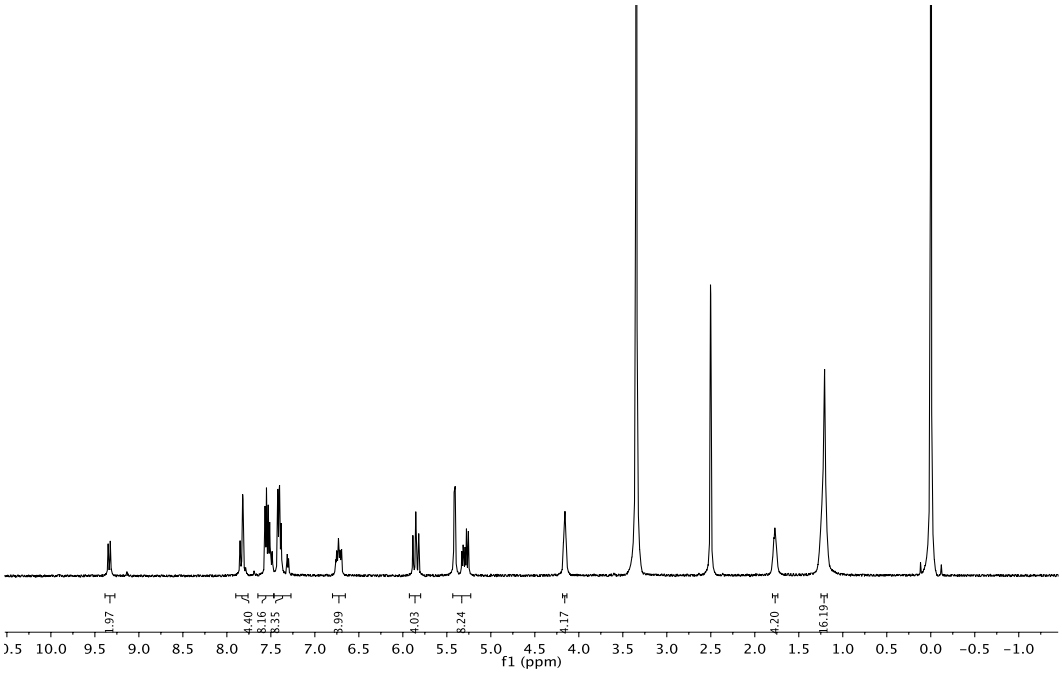

Figure B2. ^{1}H NMR spectrum of the [$(VBIm)_2C_{12}$] 2[SS] crosslinker: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.90 – 7.76 (m, 4H), 7.65 – 7.47 (m, 8H), 7.40 (dd, 8H), 6.73 (dt, 4H), 5.93 – 5.80 (m, 4H), 5.43 – 5.23 (m, 8H), 4.16 (s, 4H), 1.77 (s, 4H), 1.21 (s, 16H).

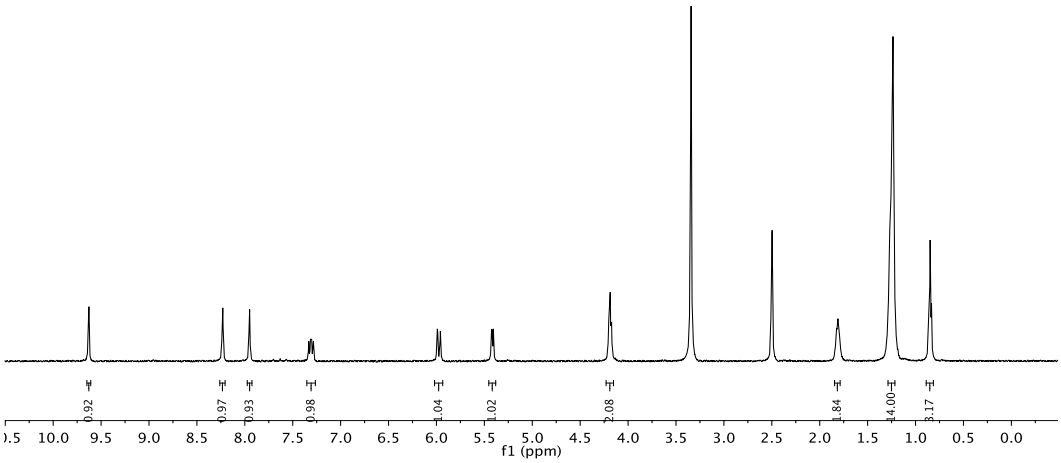

Figure B3. ^{1}H NMR spectrum of the [$VImC_{10}$][Cl] monomer: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.63 (s, 1H), 8.23 (t, 1H), 7.95 (t, 1H), 7.35 – 7.26 (m, 1H), 5.97 (dt, 1H), 5.42 (dt, 1H), 4.23 – 4.15 (m, 2H), 1.82 (d, 2H), 1.25 (d, 14H), 0.89 – 0.81 (t, 3H).

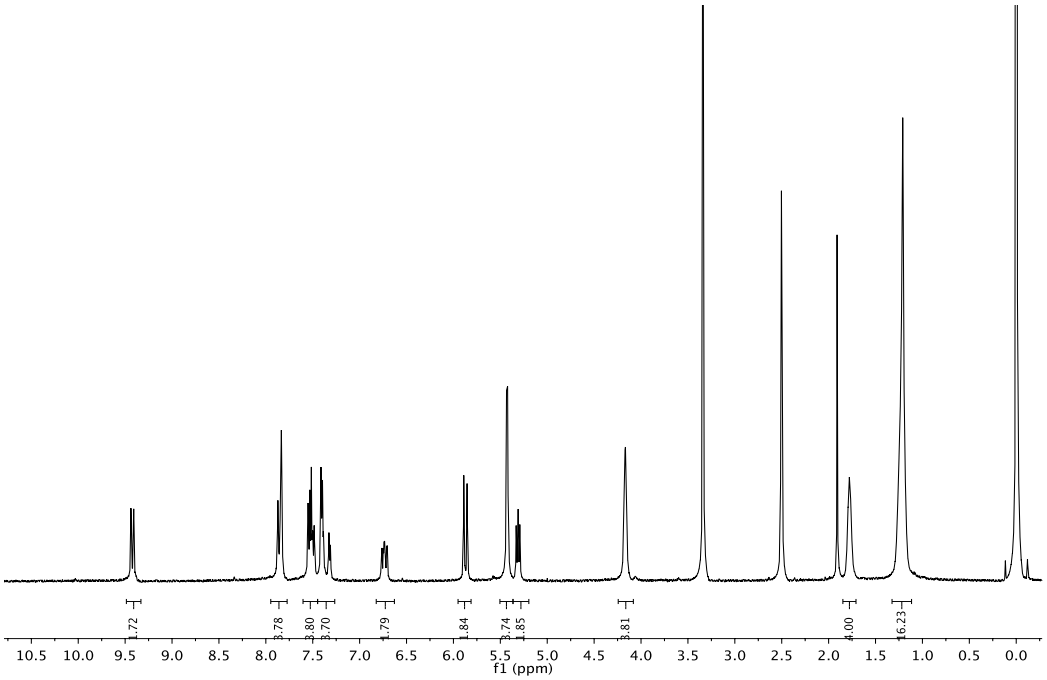

Figure B4. ^{1}H NMR spectrum of the [$(VBIm)_2C_{12}$] 2[Cl] crosslinker: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.42 (d, 2H), 7.95 – 7.77 (m, 4H), 7.60 – 7.45 (m, 4H), 7.40 (dt, 4H), 6.74 (ddd, 2H), 5.87 (d, 2H), 5.43 (d, 4H), 5.31 (dd, 2H), 4.17 (td, 4H), 1.78 (s, 4H), 1.21 (s, 16H).

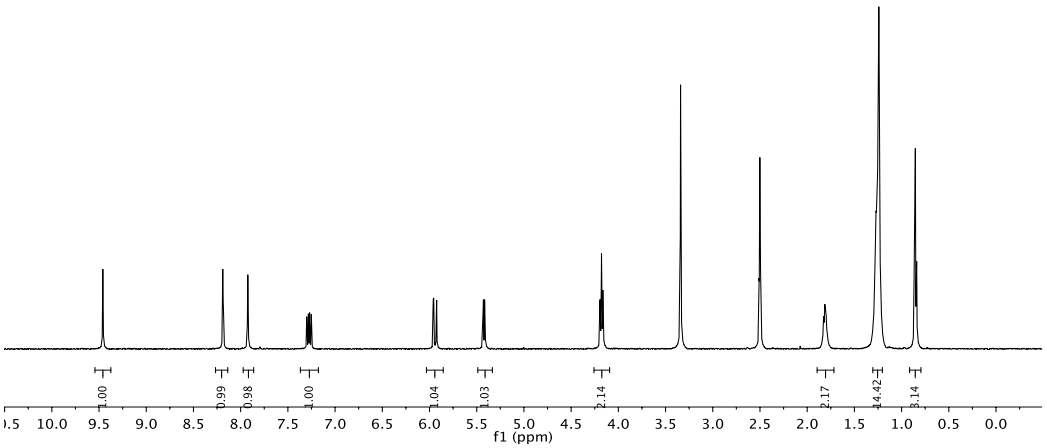

Figure B5. ^{1}H NMR spectrum of the [$VImC_{10}$][NTf_2] monomer: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.46 (s, 1H), 8.19 (t, 1H), 7.92 (t, 1H), 7.28 (dd, 1H), 5.94 (dd, 1H), 5.42 (dd, 1H), 4.18 (t, 2H), 1.81 (p, 2H), 1.25 (d, 14H), 0.96 – 0.74 (t, 3H).

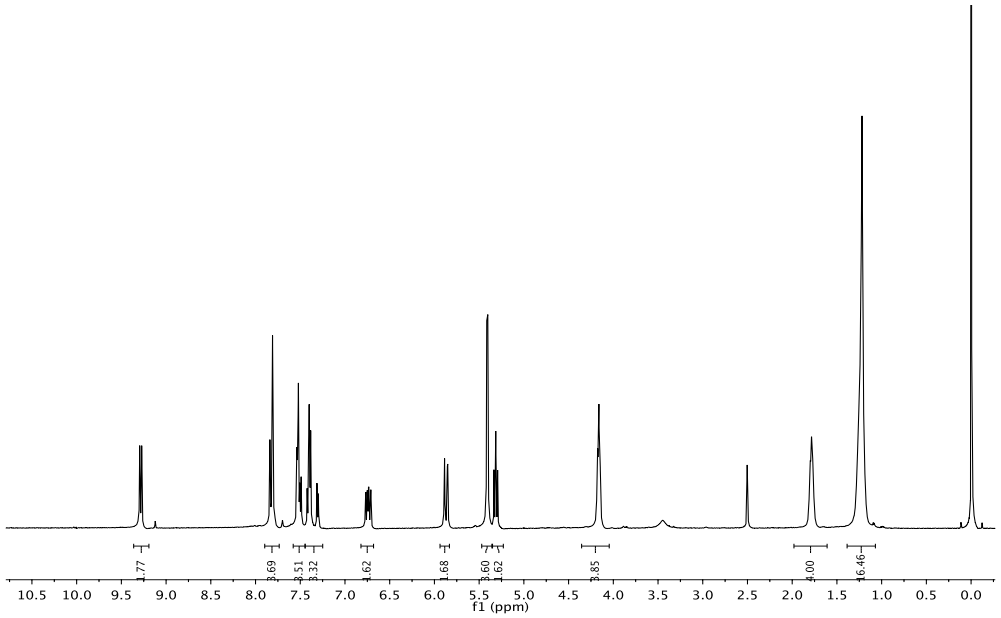

Figure B6. ^{1}H NMR spectrum of the $[(VBIm)_2C_{12}]$ 2$[NTf_2]$ crosslinker: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.28 (dt, 2H), 7.90 – 7.74 (m, 4H), 7.58 – 7.45 (m, 4H), 7.45 – 7.25 (m, 4H), 6.74 (ddd, 2H), 5.87 (ddd, 2H), 5.41 (d, 4H), 5.31 (ddd, 2H), 4.16 (td, 4H), 1.78 (s, 4H), 1.23 (d, 16H).

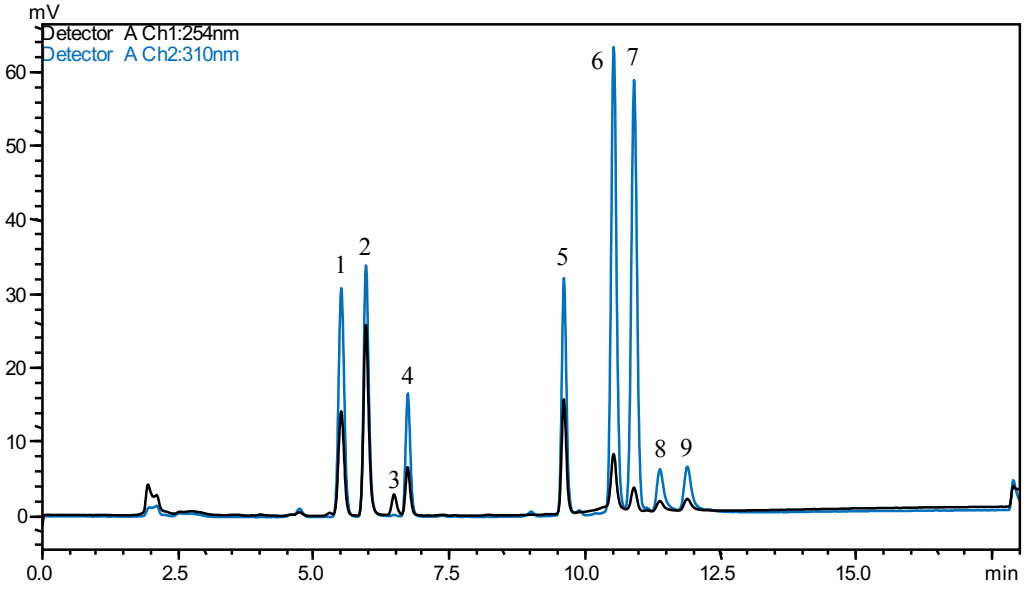

Figure B7. A representative chromatogram of the target analytes after extraction at optimal conditions with Fiber **1** from an aqueous solution containing 25% NaCl (w/v). Concentration of all analytes: 200 µg L^{-1}. (1) Ethyl 2-cyano-3,3-diphenylacrylate; (2) Oxybenzone; (3) Avobenzone; (4)Benzyl-salicylate; (5) Octocrylene; (6) 2-Ethylhexyl 4-methoxycinamate; (7) 2-Ethylhexyl 4-(dimethylamino)benzoate; (8) 2-Ethylhexylsalicylate; (9) Homosalate.

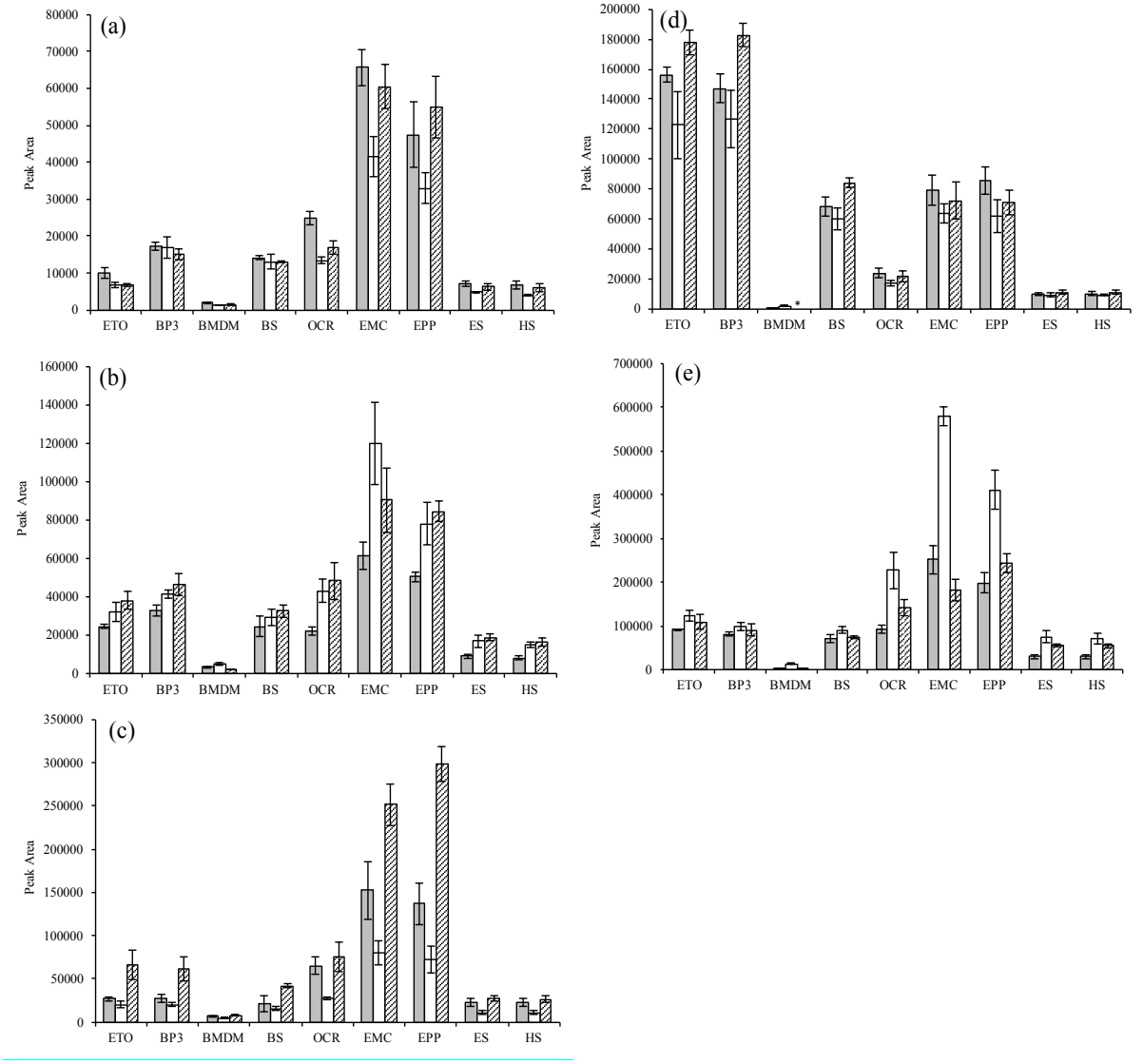

Figure B8. Comparison of desorption solvent performance for (a) Fiber **1**, (b) Fiber **2**, (c) Fiber **3**, (d) PDMS/DVB, and (e) PDMS fibers. (▒) Methanol, (□) acetonitrile, and (▨) acetone. Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 0 % NaCl (w/v); stir rate: 500 rpm; extraction time: 30 min; desorption volume: 40 μL; desorption time: 15 min.

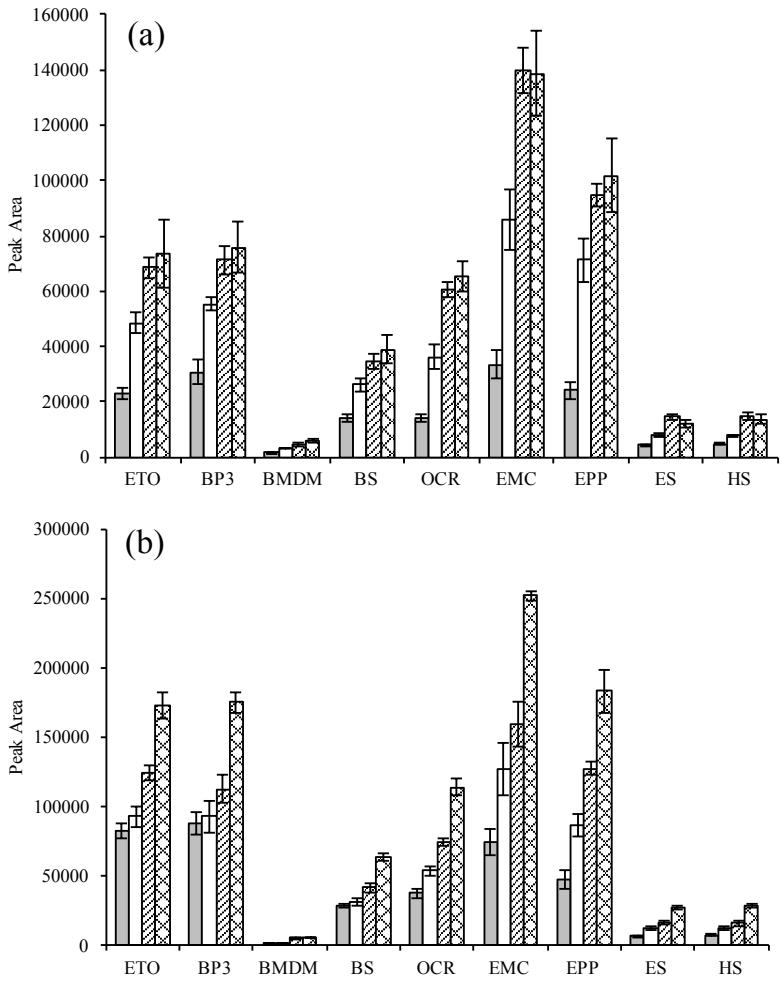

Figure B9. Influence of stir rate on analyte extraction efficiencies using (a) Fiber **1** and (b) PDMS/DVB fiber. (▩) 300 rpm, (□) 500 rpm, (▨) 700 rpm, and (▧) 900 rpm. Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 25 % NaCl (w/v); extraction time: 30 min; desorption solvent: methanol; desorption volume: 40 μL; desorption time: 15 min.

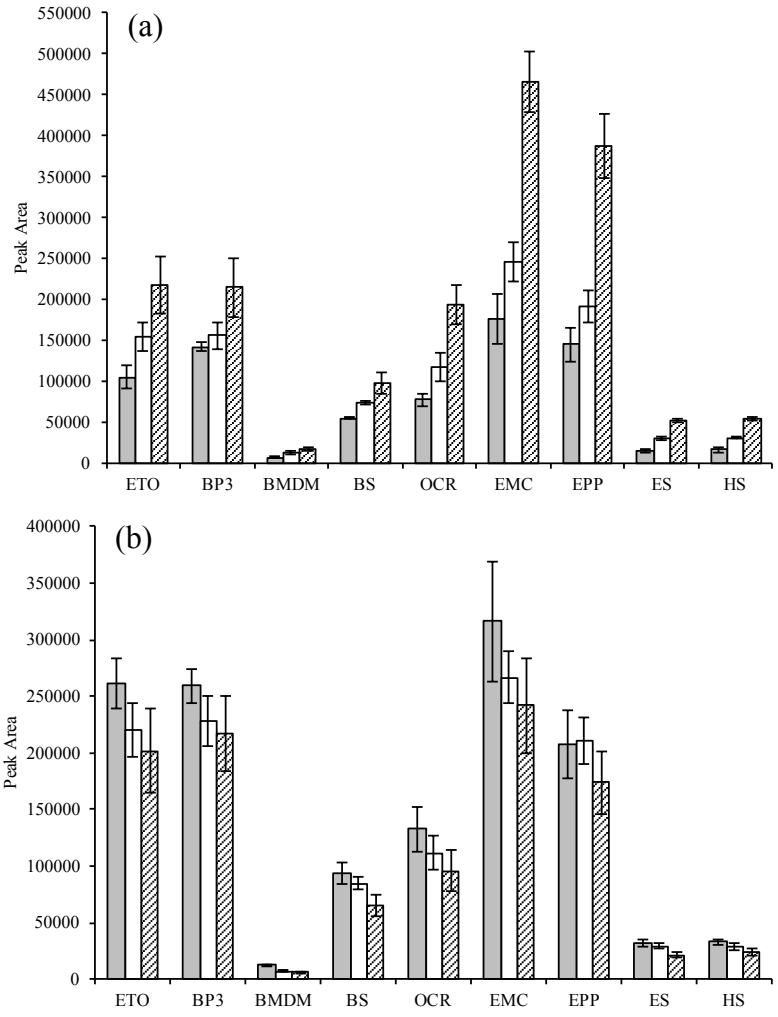

Figure B10. Influence of desorption solvent volume using (a) Fiber **1** and (b) PDMS/DVB fiber. (▩) 30 µL, (□) 40 µL, and (▨) 50 µL of the optimal desorption solvent. Experimental conditions (n = 3): analyte concentration: 200 µg L^{-1}; salt concentration: 25 % NaCl (w/v); stir rate: 700 rpm (Fiber **1**) and 900 rpm (PDMS/DVB); extraction time: 75 min (Fiber **1**) and 60 min (PDMS/DVB); desorption solvent: methanol; desorption time: 15 min.

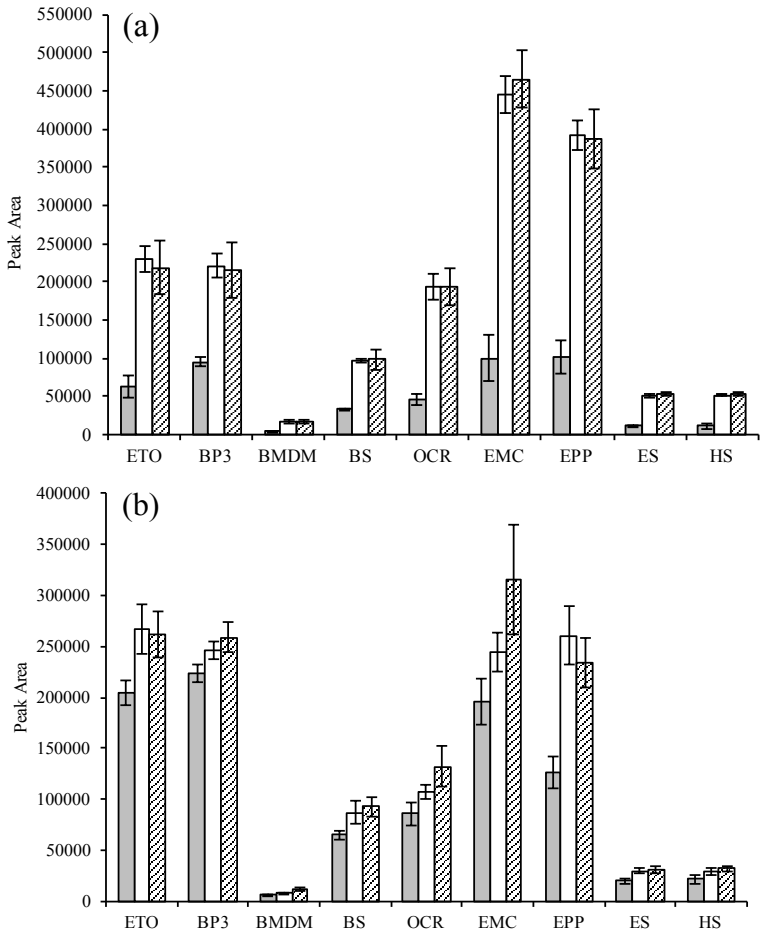

Figure B11. Influence of desorption time using (a) Fiber **1** and (b) PDMS/DVB fiber. (▒) 5 min, (□) 10 min, and (▨) 15 min of desorption. Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 25 % NaCl (w/v); stir rate: 700 rpm (Fiber **1**) and 900 rpm (PDMS/DVB); extraction time: 75 min (Fiber **1**) and 60 min (PDMS/DVB); desorption solvent: methanol; desorption volume: 50 μL (Fiber **1**) and 30 μL (PDMS/DVB).

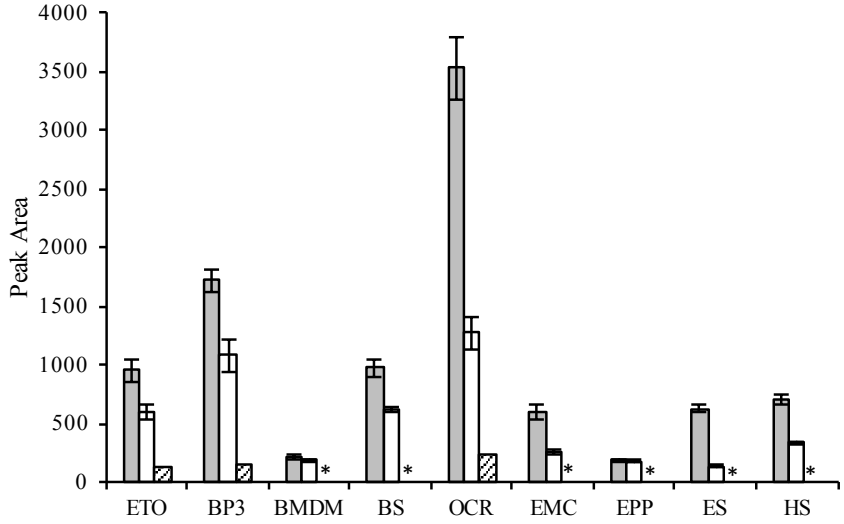

Figure B12. Comparison of peak areas after the second desorption step for testing of the analyte carryover using Fiber **1**. (▩) 2 min, (□) 3 min, and (▨) 5 min of the second desorption time. Experimental conditions (n = 3): analyte concentration: 200 μg L^{-1}; salt concentration: 25 % NaCl (w/v); stir rate: 700 rpm; extraction time: 75 min; desorption solvent: methanol; desorption volume: 50μL; desorption time: 10 min. The * sign denotes that no peaks were detected after 5 min of washing step.

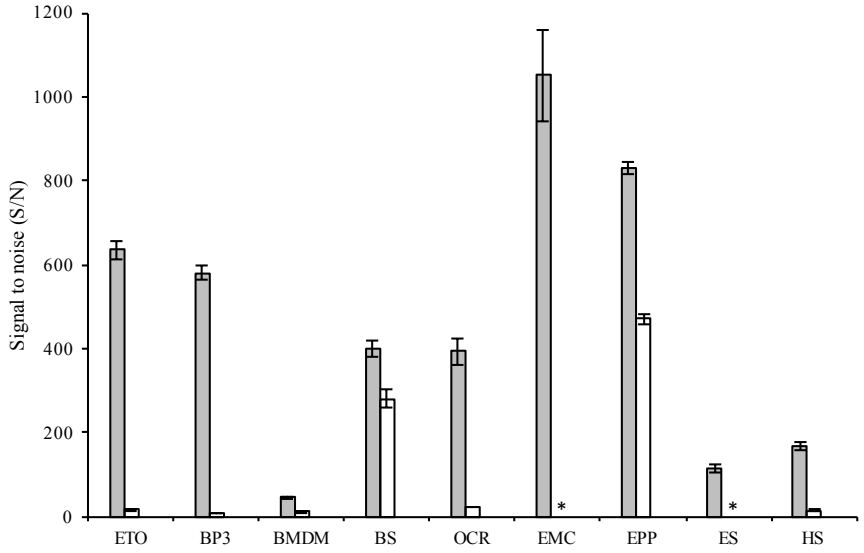

Figure B13. Signal-to-noise ratio obtained with (▩) diode array detection and (□) ESI-TOF (extracted ion chromatogram, EIC) after extraction at the optimal conditions using Fiber **1**. Concentration of all analytes: 200 μg L^{-1}. The * sign denotes that no signal was detected

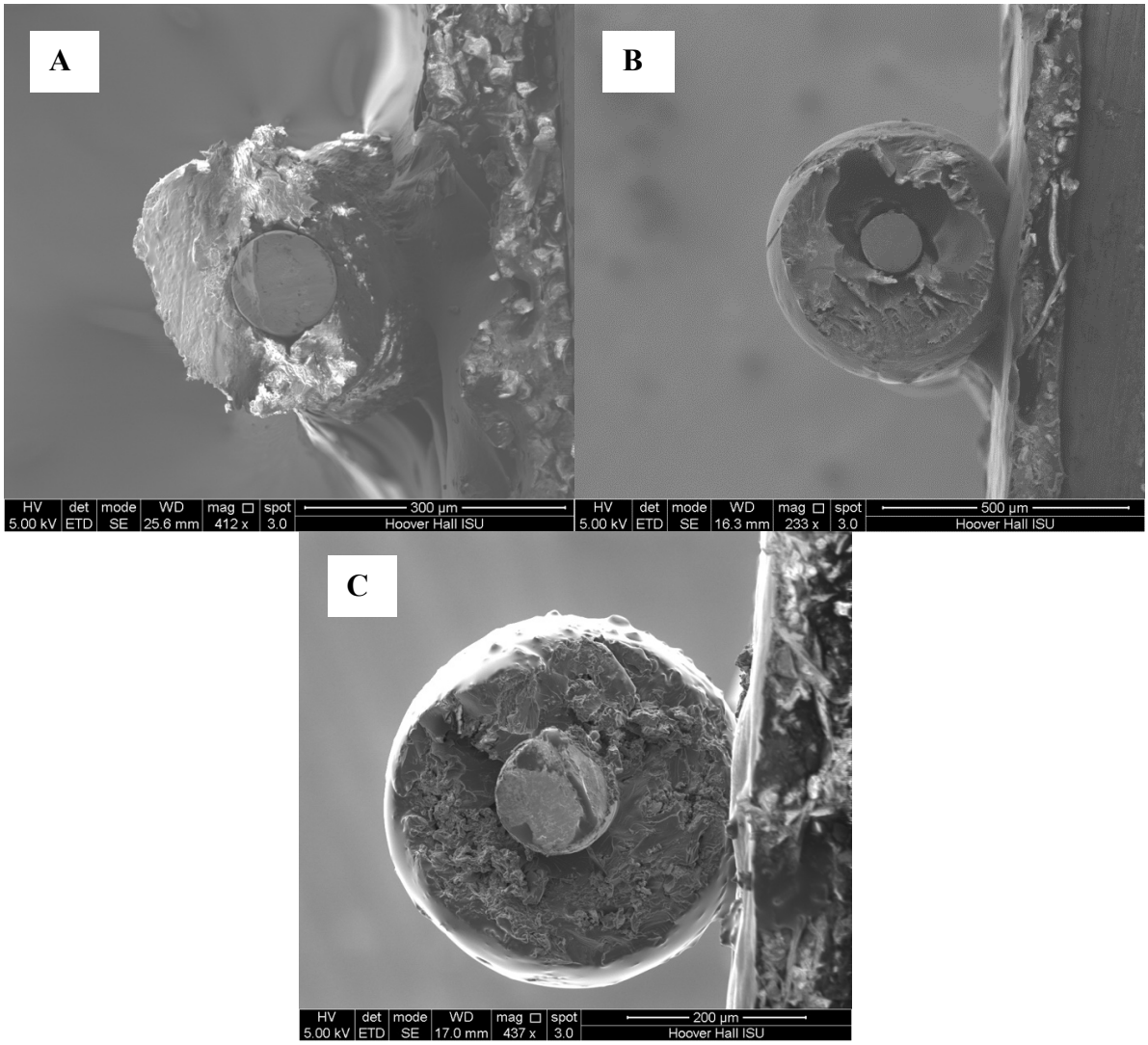

Figure B14. A scanning electron micrograph image of the (a) Fiber **1** sorbent coating after 120 extraction (from aqueous solution of 25% NaCl, w/v) and desorption cycles; (b) Fiber **2** sorbent coating after 22 extraction (in aqueous solution of 25% NaCl, w/v) and desorption cycles; (c) Fiber **3** sorbent coating after 5 extraction (in aqueous solution of 25% NaCl, w/v) and desorption cycles.

Table B1. Comparison of figures of merit with existing microextraction methods for determination of UV filters using HPLC coupled to UV detection.

Method	Common analytes	Extraction phase reusability –Y/N	Linear range (μg L^{-1})	LOD (μg L^{-1})	Salt content (w/v)	Recovery matrix	Reference
SDME[a]	BP3, OCR, EMC	N	1-150 (BP3, EMC), 10-150 (OCR)	0.11-3.00	-	River, sea, channel water	[1]
SDME[a]	BP3	N	0-100	1.30	13% NaCl	Human urine	[2]
HF-LPME[b]	BP3	N	5-1000	0.20	20% NaCl	Tap, river water	[3]
In-syringe MSA-DLLME[c]	BP3, OCR, ES, HS	N	0.6-500 (BP3) 8.5-500 (OCR) 40-500 (ES) 34-500 (HS)	0.18-11.82	-	Sea, pool water	[4]
UA-DLLME[d]	BP3	N	1-500	0.30	1% NaCl	Pool, river water	[5]
UA-DLLME[d]	BP3, ES, HS	N	5-500 (BP3) 10-500 (ES) 5-500 (HS)	0.50-5.0	-	Tap, pool, river water	[6]
On-line SPME	BP3, EPP, EMC	Y	0.25-200 (BP3) 0.5-200 (EPP) 1.0-200 (EMC)	0.06-0.13	-	Lake, river, wastewater	[7]
DI-SPME[e]	BP3, EPP, EMC, HS	Y[f]	0.2-200	0.03-0.05	5% NaCl	River, wastewater	[8]
DI-SPME[e]	9 total analytes	Y[g]	0.5-200[h]	0.10-5.00[h]	25% NaCl	Tap, pool, lake water	This paper

[a] Single-drop microextraction
[b] Hollow fiber liquid-phase microextraction
[c] Magnetic stirring assisted dispersive liquid-liquid microextraction
[d] Ultrasound assisted dispersive liquid-liquid microextraction
[e] Direct immersion solid-phase microextraction
[f] Reported reusability for up to 200 extractions
[g] Reusable for up to 120 extraction-desorption cycles
[h] Refer to Table 2 for individual values

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